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THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND UNSATURATED COMPOUNDS CONTAINING ALKOXYL GROUPS.

BY GRACE POTTER REYNOLDS.

In the work on reactions between organic magnesium compounds and unsaturated compounds, a careful study has been made of the effect of hydrocarbon residues in substances that contain the chain C : C.C : O.[1] As a result it is possible to predict the mode of addition to a substance with any combination of hydrocarbon residues attached to this chain.

The influence of a few other groups has also been studied. Bromcinnamic ester[2] gives products analogous to those obtained from cinnamic ester, the principal effect of the bromine atom being to diminish the tendency toward formation of secondary products. In the reaction with α-cyancinnamic ester[3] and benzalmalonic ester,[4] however, the cyanogen and carboxethyl groups in the α position prevent the replacement of the alkoxyl group, and, consequently, only 1,4-addition products are obtained.

In continuation of this work it was desirable to study the

[1] THIS JOURNAL, **33**, 153; **36**, 529; **38**, 511.
[2] *Ibid.*, **33**, 35.
[3] *Ibid.*, **33**, 333.
[4] *Ibid.*, **34**, 132.

effect of β substituents, other than hydrocarbon residues, on the reaction between unsaturated compounds and organic magnesium compounds. The principal object of this research was to determine the influence of alkoxyl groups on the mode of addition in these reactions. It was convenient to include an investigation as to the possibility of using the Grignard reagent for the study of keto-enol tautomerism.

Methylmagnesium iodide has been successfully used for the quantitative estimation of the hydroxyl group in a large number of compounds; few of these, however, are substances exhibiting keto-enol tautomerism. In the first paper on the quantitative determination of the hydroxyl group by means of the Grignard reagent, Tschugaeff[1] states that a series of tautomeric substances behaved like hydroxyl compounds toward methylmagnesium iodide. Later, in a general quantitative investigation of the action of the Grignard reagent on substances containing "active" hydrogen, Zerewitnoff[2] included a few tautomeric compounds. His results indicated that they reacted as enols. As these results are not conclusive, it seemed desirable to attempt a systematic investigation in order to decide whether methylmagnesium iodide can be used as a reagent for the study of keto-enol desmotropism.

The reagents most frequently used in recent work on this subject are acetyl chloride, acetic anhydride, phenyl isocyanate and tertiary amines.[3] With tertiary amines the reactions take place at a comparatively low temperature, but with acetyl chloride and acetic anhydride it is generally necessary to heat to a high temperature and, sometimes, even in sealed tubes, to bring about a reaction. The Grignard reaction ordinarily takes place instantaneously and at a very low temperature; it seemed possible, therefore, that methylmagnesium iodide might be well adapted to a study of keto-enolization. The results obtained with tautomeric compounds may be summed up as follows:

[1] Ber. d. chem. Ges., **35**, 3912.
[2] *Ibid.*, **40**, 2023.
[3] Ann. Chem. (Liebig), **363**, 36.

1. The amount of enolic modification cannot be determined by measuring the volume of methane obtained by treating a known weight of substance with excess of methylmagnesium iodide; when ethyl ether is used as a medium its high vapor tension interferes with the accurate estimation of the gas volume, and when amyl ether is substituted for ethyl ether the reaction goes so slowly that the anticipated advantage of an instantaneous reaction is lost.

2. The relative amounts of enolic and ketonic modifications cannot be determined by a study of the products obtained when tautomeric substances are treated with the Grignard reagent. This is shown by a consideration of the reaction between phenylmagnesium bromide and the diethyl ester of hydroxymethylenemalonic acid. The sole product of this reaction is benzalmalonic ester, formed by the action of two molecules of the Grignard reagent on one molecule of the ester:

$$C_2H_2O(COOC_2H_5)_2 + 2C_6H_5MgBr + H_2O = C_6H_5CH : C(COOC_2H_5)_2 + 2Mg(OH)Br + C_6H_6.$$

This reaction can be interpreted on the assumption that the ester is an enol, as maintained by Claisen:

$$CH(OH) : C(COOC_2H_5)_2 + 2C_6H_5MgBr \longrightarrow C_6H_5CH(OMgBr)—C(OMgBr) : C(OC_2H_5)(COOC_2H_5)$$

On decomposition, the magnesium derivative would give the diethyl ester of phenylhydroxymethylmalonic acid, and this, by loss of one molecule of water, benzalmalonic ester:

$$C_6H_5CH(OMgBr)—C(OMgBr)(COOC_2H_5) : C(OC_2H_5) \longrightarrow$$

$$C_6H_5CH(OH)—CH(COOC_2H_5)_2 \longrightarrow C_6H_5CH : C(COOC_2H_5)_2.$$

The reaction can be interpreted equally well on the assump-

tion that the ester is an aldehyde, the product being a result of 1,2-addition to carbonyl:

$$HCCH(COOC_2H_5)_2 + C_6H_5MgBr \longrightarrow$$
$$\underset{\underset{O}{\|}}{}$$

$$C_6H_5CH(OMgBr)—CH(COOC_2H_5)_2 \longrightarrow$$

$$C_6H_5CH(OH)—CH(COOC_2H_5)_2 \longrightarrow$$

$$C_6H_5CH : C(COOC_2H_5)_2.$$

One of these interpretations requires the use of twice as much reagent as the other, but this difference cannot serve as a means of distinguishing between the two, because a large excess is needed in order to have a clean reaction.

These considerations led me to conclude that the Grignard reagent cannot be used for the study of tautomerism.

The influence of alkoxyl groups was studied with the diethyl ester of ethoxymethylenemalonic acid. In structure, this substance may be compared with benzalmalonic ester, which differs from it only in having a phenyl group in place of an ethoxyl group. With phenylmagnesium bromide, benzalmalonic ester gives the diethyl ester of β,β-diphenylmethylmalonic acid.[1] This is the final product obtained in the reaction between the diethyl ester of ethoxymethylenemalonic acid and phenylmagnesium bromide. In the case of the ethoxy derivative, there are several ways of accounting for the formation of this product.

1. Benzalmalonic ester may be formed by the replacement of the ethoxyl group by a phenyl group; this ester would combine with a second molecule of phenylmagnesium bromide and form the magnesium derivative of β,β-diphenylmethylmalonic ester:

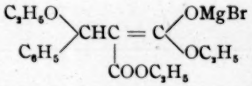
$$C_6H_5CH : C(COOC_2H_5)_2 + C_6H_5MgBr \longrightarrow$$

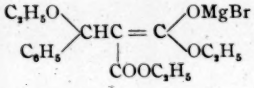
$$(C_6H_5)_2CHC(COOC_2H_5) = C(OMgBr)(OC_2H_5).$$

[1] This Journal, **34**, 132.

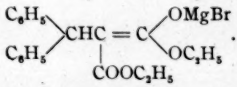
2. The order of the reactions may be reversed and 1,4-addition may take place with subsequent replacement of the ethoxyl group with a phenyl group:

$$C_2H_5OCH : C(COOC_2H_5)_2 + C_6H_5MgBr \longrightarrow$$



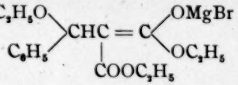


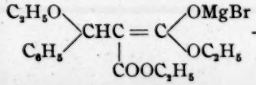
$$+ C_6H_5MgBr \longrightarrow$$



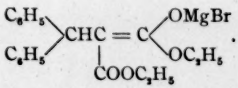
3. Or the mechanism may be represented by the following equations, likewise involving the intermediate formation of benzalmalonic ester:

$$C_2H_5OCH : C(COOC_2H_5)_2 + C_6H_5MgBr \longrightarrow$$





$$\longrightarrow C_6H_5CH : C(COOC_2H_5)_2 \longrightarrow$$



In order to get some evidence as to the mechanism of this reaction, β-ethoxypropiophenone was studied for the purpose of determining whether the ethoxyl group in saturated ketones is replaceable. The ketone gives with both phenylmagnesium bromide and ethylmagnesium bromide solely 1,2-addition products:

$$C_2H_5OCH_2CH_2COC_6H_5 + C_6H_5MgBr + H_2O = C_2H_5OCH_2CH_2C(C_6H_5)_2OH + Mg(OH)Br.$$

This reaction, therefore, is of little assistance in interpreting the action of phenylmagnesium bromide on the ethoxymethylene ester.

More significant are the reactions of β-ethoxybenzalacetophenone which has a phenyl group attached to the same carbon atom that holds the ethoxyl group. The products of the reactions between this ketone and organic magnesium compounds depend upon the concentration of the magnesium compound; in concentrated solution only addition takes place, in dilute solution addition and subsequent replacement of the ethoxyl group. This difference is due to the insolubility of the magnesium derivatives first formed; if a small amount of ether is present these magnesium derivatives appear as white crystalline solids and do not enter into further reaction with the Grignard reagent.

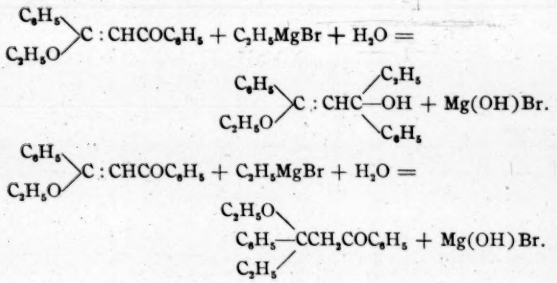
In concentrated solution with phenylmagnesium bromide β-ethoxybenzalacetophenone gives solely a 1,2-addition product:

$$(C_6H_5)(C_2H_5O)C:CHCOC_6H_5 + C_6H_5MgBr = (C_6H_5)(C_2H_5O)C:CHC(C_6H_5)_2OMgBr$$

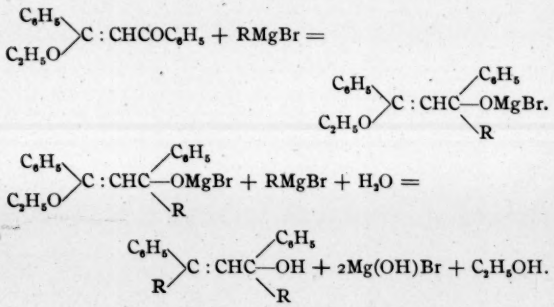
$$(C_6H_5)(C_2H_5O)C:CHC(C_6H_5)_2OMgBr + H_2O = (C_6H_5)(C_2H_5O)C:CHC(C_6H_5)_2OH + Mg(OH)Br.$$

Though with phenylmagnesium bromide 1,2-addition only

takes place, with ethylmagnesium bromide both 1,2- and 1,4-addition products result:



In dilute solution with both phenylmagnesium bromide and ethylmagnesium bromide the ketone gives 1,2-addition products with a hydrocarbon residue in place of the ethoxyl group:



The study of β-ethoxybenzalacetophenone establishes beyond doubt the mechanism of the reaction between organic magnesium compounds and unsaturated compounds that have an alkoxyl group in the β position; the first step is addition, either 1,2 to carbonyl or 1,4 to the conjugated

system; the alkoxyl group of the resulting substance may or may not be replaced later by a hydrocarbon residue.

The influence of the β-ethoxyl group upon the mode of addition in the Grignard reaction is approximately the same as that of the phenyl group. This is shown by the following table in which the amount of 1,4-addition product obtained with β-ethoxybenzalacetophenone is compared with the amount of 1,4-addition product obtained with related ketones. The numbers in Columns 1 and 2 express the percentage of ketone represented by the amount of 1,4-addition product that resulted:

	With C_6H_5MgBr.	With C_2H_5MgBr.
$C_6H_5CH : CHCOC_6H_5$	94	99
$(CH_3)_2C : CHCOC_6H_5$	mainly	..
$(C_6H_5)(CH_3)C : CHCOC_6H_5$	41	44
$(C_6H_5)(C_2H_5O)C : CHCOC_6H_5$	0	45
$(C_6H_5)_2C : CHCOC_6H_5$	0	18
$(CH_3)_2C : CHCOCH_3$	0	0

EXPERIMENTAL.

For the purpose of deciding whether the Grignard reagent can be used for the quantitative estimation of an enolic modification, it seemed best to start with a substance that normally reacts as enol. Accordingly formylethylphenyl ketone was chosen for the investigation. This hydroxymethylene ketone, moreover, is well adapted to the problem because of its comparative stability and because, in the method of procedure adopted, manipulation is less difficult with a solid substance.

Experiments with Formylethylphenyl Ketone.

Formylethylphenyl ketone was prepared by the method

of Claisen,[1] but the sodium ethylate, used as a condensing agent, was made by suspending sodium wire in absolute ether and adding the calculated amount of absolute alcohol. Difficulty was experienced in obtaining the ketone pure by recrystallization from dilute alcohol as recommended by Claisen. It was purified with the greatest ease, however, by distillation under diminished pressure; boiling point, 155° (25 mm.). The solid, washed with ether to free it of the last trace of coloring matter, was used for the quantitative estimation of an enolic modification.

Hibbert and Sudborough,[2] who developed a method for the quantitative determination of hydroxyl with methylmagnesium iodide, recommended the use of amyl ether as a medium and pyridine as a solvent. These investigators found it necessary to work in an atmosphere of some indifferent gas, owing to the absorption of air by the Grignard reagent. Zerewitnoff, however, found that the method can be used without excluding air from the apparatus.

My method of procedure was essentially that suggested by Zerewitnoff. It was difficult to keep the pyridine dry during the necessary manipulation and also to finish a quantitative determination before an appreciable amount of air was absorbed by the methylmagnesium iodide. Errors in the estimation of the volume of methane due to these experimental difficulties would be opposite in sign and might easily balance each other. Trial reactions with menthol gave results agreeing with those obtained by Zerewitnoff, though a blank test showed that the pyridine was not dry. It was necessary, therefore, to work in an atmosphere of nitrogen if the determinations were to be trusted. In amyl ether the speed of the reaction is very slow This was shown by the different rates of absorption of air with ethyl ether and amyl ether as media; also by the failure of formylethylphenyl ketone to react with methylmagnesium iodide in the absence of pyridine in amyl ether though the reaction in ethyl ether is instantaneous. This difference in reactivity in the two ethers is

[1] Ber. d. chem. Ges., **22**, 3277.
[2] J. Chem. Soc., **85**, 933.

not due to solubility relations because the ketone is equally insoluble in both of them. These observations showed that this method cannot be used for the quantitative estimation of the hydroxyl group in the hydroxymethylene ketone.

For the purpose of deciding whether the nature of the products obtained in the Grignard reaction can serve for a determination of the relative amounts of ketonic and enolic modifications, it was necessary to use substances with a substituent in the α position in order to avoid complications owing to secondary reactions. For this study, also, it seemed best to select substances that normally react as enols. The diethyl ester of hydroxymethylenemalonic acid and formylethylphenyl ketone, therefore, were chosen as unsaturated compounds most suitable for this work.

Experiments with Diethyl Hydroxymethylenemalonate.[1]

An ethereal solution of this ester was added to an excess of phenylmagnesium bromide. The product was treated in the usual way and fractioned under diminished pressure. A colorless liquid distilled at 185° (16 mm.); this is the boiling point of benzalmalonic ester. Since benzalmalonic ester decomposes on hydrolysis, the identity of the product was established by treatment with phenylmagnesium bromide. The saturated ester obtained in this reaction gave, on saponification with alcoholic potassium hydroxide, monoethyl diphenylmethylmalonate, which was identified by comparison with a specimen on hand.

The ester was allowed to react with ethylmagnesium bromide and the product isolated as in the previous case. It boiled at 117°–120° (14 mm.). Analysis showed that the liquid was impure. As it was impracticable to try to purify it with the small amount of material at my disposal, an indirect method of identification was attempted. If the mode of addition with ethylmagnesium bromide is the same as with phenylmagnesium bromide, the product is propylidenemalonic ester; this would react with phenylmagnesium bromide and form the diethyl ester of phenylethylmethylmalonic acid:

[1] Ann. Chem. (Liebig), **297**, 78.

$$C_2H_5CH : C(COOC_2H_5)_2 + C_6H_5MgBr + H_2O = \begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}\!\!>\!CHCH(COOC_2H_5)_2 + Mg(OH)Br.$$

Since it is very difficult to prepare the hydroxymethylene compound, this saturated ester was made from benzalmalonic ester, which can be procured in quantity with comparative ease:

$$C_6H_5CH : C(COOC_2H_5)_2 + C_2H_5MgBr + H_2O = \begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}\!\!>\!CHCH(COOC_2H_5)_2 + Mg(OH)Br.$$

Diethyl Phenylethylmethylmalonate, $\begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}\!\!>\!CHCH(COOC_2H_5)_2$. —An ethereal solution of benzalmalonic ester was added to an excess of ethylmagnesium bromide. The magnesium derivative was decomposed in the usual way and the resulting liquid fractioned under diminished pressure. A colorless product distilled at 187°–188° (22 mm.); the yield was quantitative.

Analysis:

0.1727 gram substance gave 0.4370 gram CO_2 and 0.1144 gram H_2O.

	Calculated for $C_{16}H_{22}O_4$.	Found.
C	69.06	69.01
H	7.91	7.36

Phenylethylmethylmalonic Acid, $\begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}\!\!>\!CHCH(COOH)_2$. — Strong aqueous potassium hydroxide was added to an alcoholic solution of the ester and the mixture was heated for two hours. On evaporating the alcohol and acidifying the aqueous solution, glistening white plates were precipitated. The acid was purified by recrystallization from warm water. It is very soluble in alcohol, ether and acetone. It crystallizes with one molecule of water and melts at 74°.

Analysis:

0.1122 gram substance lost 0.0083 gram H_2O at 100°.

0.1836 gram substance gave 0.4050 gram CO_2 and 0.1050 gram H_2O.

	Calculated for $C_{12}H_{14}O_4.H_2O$.	Found.
H_2O	7.50	7.39
C	60.00	60.16
H	6.66	6.35

This acid was shown to be a malonic acid by the product it gave on decomposition. When the dibasic acid was kept at 150° until evolution of carbon dioxide ceased, phenylethylpropionic acid, $\begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}\!\!>\!CHCH_2COOH$, was obtained. It was purified by recrystallization from ether. It is very soluble in alcohol and ether and melts at 66°.

Analysis:

0.1669 gram substance gave 0.4533 gram CO_2 and 0.1176 gram H_2O.

	Calculated for $C_{11}H_{14}O_2$.	Found.
C	74.15	74.07
H	7.86	7.82

The substance obtained in the reaction between the hydroxymethylene ester and ethylmagnesium bromide was treated with phenylmagnesium bromide. The product was isolated in the usual way and saponified with aqueous potassium hydroxide. An acid was obtained but it could not be made to solidify even by seeding with phenylethylmethylmalonic acid and its identity was not established. It is probable that in the time taken for carrying out the above series of reactions, the product obtained from the hydroxymethylene ester had decomposed to such an extent that it gave a mixture of substances on treatment with phenylmagnesium bromide.

Experiments with Formylethylphenyl Ketone.

Reaction with Phenylmagnesium Bromide.—The solid ketone was allowed to react with phenylmagnesium bromide. The product was treated in the usual way and the resulting sub-

stance fractioned under diminished pressure. A yellow liquid distilled at 210°–213° (23 mm.), which is the boiling point of benzalpropiophenone.

$$\begin{matrix} CH : CCOC_6H_5 \\ | \quad\; | \\ OH \quad CH_3 \end{matrix} + C_6H_5MgBr + H_2O \longrightarrow C_6H_5CH : \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}COC_6H_5.$$

The substance was identified by its hydrazone, melting at 127°–128°, and by the product that it gave with phenylmagnesium bromide. The diphenylisobutyrophenone obtained in this reaction was identified by comparison with a specimen on hand.

Reaction with Ethylmagnesium Bromide.—Solid hydroxymethylene ketone was added to a solution of ethylmagnesium bromide, the magnesium derivative decomposed in the usual way, and the resulting yellow liquid distilled under diminished pressure. The product boiled at 137°–142° (16 mm.). As repeated distillations failed to give a pure substance, 100 grams of material were accumulated and subjected to a systematic fractionation, first under diminished pressure and then at atmospheric pressure. The product lost water very gradually when heated to 130°, but even after six distillations a cloudy appearance of the distillate indicated that water was still being driven off. It was not practicable, therefore, to eliminate it completely by distillation.

If the mode of addition with ethylmagnesium bromide was the same as with phenylmagnesium bromide, the reaction would be represented as follows:

$$\begin{matrix} CH : CCOC_6H_5 \\ | \quad\; | \\ OH \quad CH_3 \end{matrix} + C_2H_5MgBr + H_2O \longrightarrow \begin{matrix} C_2H_5CH.CHCOC_6H_5. \\ | \quad\; | \\ OH \quad CH_3 \end{matrix}$$

This saturated ketone, on loss of water, would give propylidenethylphenyl ketone, $C_2H_5CH : \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}COC_6H_5$. An analogous reaction is the formation of ethylidenacetone from hydracetylacetone.[1] As in this case water was eliminated by

[1] Ann. Chem. (Liebig), **306**, 324.

the action of acetic anhydride, the product obtained from the hydroxymethylene ketone was subjected to the same treatment. Analysis of the resulting substance, however, indicated that it was not pure propylidenethylphenyl ketone. That it was this ketone, slightly contaminated by saturated hydroxyl ketone or some material which could not be separated by distillation, was established by two addition reactions.

Reaction with Bromine.—The liquid was dissolved in carbon bisulphide, and the solution cooled with a freezing mixture and treated with a solution of bromine in the same solvent. On evaporation of the solvent in a draught the product was left as a solid and was purified by recrystallization from alcohol. The firm, white needles are soluble in ether, acetone and chloroform, less so in methyl alcohol; they melt at 67°.

Analysis:

0.1566 gram substance gave 0.2478 gram CO_2 and 0.0585 gram H_2O.

	Calculated for $C_{12}H_{14}OBr_2$.	Found.
C	43.11	43.15
H	4.19	4.15

As this substance is a dibromide, it proves the presence of an unsaturated ketone, and the excellent yield shows that the liquid is chiefly propylidenethylphenyl ketone.

Reaction with Phenylmagnesium Bromide.—For further evidence as to the structure of the product obtained from the action of ethylmagnesium bromide on formylethylphenyl ketone, the reaction between the product and phenylmagnesium bromide was studied. If the substance is chiefly propylidenethylphenyl ketone, it should react with phenylmagnesium bromide and give ethylphenylisobutyrophenone. For purposes of comparison, the ketone was prepared from benzalpropiophenone.

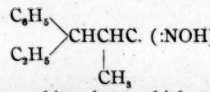
Ethylphenylisobutyrophenone, $\begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}\!\!>\!CHCHCOC_6H_5$. — An
$\quad\quad\quad

the magnesium derivative a yellow liquid separated and was distilled under diminished pressure. It boiled at 202°–204° (20 mm.). After several days the liquid deposited crystals, which were purified by dissolving them in methyl alcohol at room temperature and cooling the solution in a freezing mixture. The fine white needles melt at 60°.5 and are readily soluble in alcohol, ether, acetone and chloroform

Analysis:

0.1591 gram substance gave 0.5018 gram CO_2 and 0.1136 gram H_2O.

	Calculated for $C_{18}H_{20}O$.	Found.
C	85.71	86.01
H	7.93	7.93

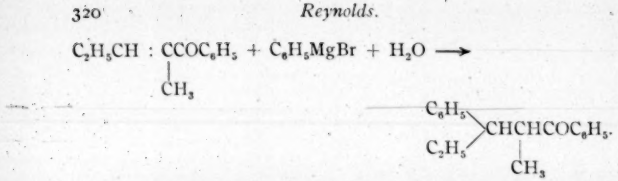
The *oxime*,  crystallizes from alcohol in heavy, white plates which melt at 119°.

Analysis:

0.1511 gram substance gave 0.4487 gram CO_2 and 0.1100 gram H_2O.

	Calculated for $C_{18}H_{21}ON$.	Found.
C	80.89	80.98
H	7.86	8.08

The product obtained from the reaction with formylethylphenyl ketone, when treated with phenylmagnesium bromide, gave a liquid that boiled at the same temperature as ethylphenylisobutyrophenone and solidified in contact with a crystal of this substance. As this solid was identical with that obtained by treating benzalpropiophenone with ethylmagnesium bromide, this established the structure of the unsaturated substance in question.

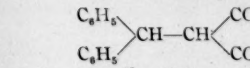


The two addition reactions show that the product is composed mainly of propylidenethylphenyl ketone. As it readily gave a solid dibromide, an attempt was made to purify it by adding bromine, recrystallizing the resulting solid and then eliminating two bromine atoms with zinc or potassium iodide. Accordingly 60 grams of the liquid were treated with bromine in the same way as before. In this case, however, only a small quantity of solid product could be isolated, though the calculated amount had been obtained from 2 grams of unsaturated ketone. The different result with a large quantity of material might be due to slight variations in the conditions of the reactions; since the dibromketone contains two unequal asymmetric carbon atoms, isomeric products difficult to separate were doubtless formed. The attempt to purify the unsaturated ketone by this method was therefore unsuccessful.

Experiments with Diethyl Ethoxymethylenemalonate.[1]

Reaction with Phenylmagnesium Bromide.—The ester was allowed to react with phenylmagnesium bromide. On decomposition of the product, a solid substance was obtained and identified as diethyl diphenylmethylmalonate by comparison with a specimen on hand.

Potassium Ethyl Diphenylmethylmalonate,



.—By treating this ester with alcoholic potassium hydroxide a potassium salt was obtained which was purified by recrystallization from water.

Analysis:

0.1713 gram substance gave 0.0430 gram K_2SO_4.

0.1721 gram substance gave 0.0441 gram K_2SO_4.

[1] Ann. Chem. (Liebig), **297**, 75.

	Calculated for $C_{18}H_{17}O_4K$.	Found. I.	II.
K	11.60	11.25	11.47

When this salt was acidified, monoethyl diphenylmethylmalonic acid, melting at 157°, resulted. On saponifying the ester with aqueous potassium hydroxide the corresponding dibasic acid was obtained and identified by its melting point, 190°–192° (dip), and by the fact that it lost carbon dioxide at 175° and gave β,β-diphenylpropionic acid.

Reaction with Ethylmagnesium Bromide.

Diethyl Diethylmethylmalonate, $\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!CH-CH(COOC_2H_5)_2$.

—From the reaction between the ester and ethylmagnesium bromide a colorless, mobile liquid resulted, which distilled at 138° (21 mm.). Yield, 94 per cent.

Analysis:

0.1726 gram substance gave 0.3948 gram CO_2 and 0.1429 gram H_2O.

	Calculated for $C_{12}H_{22}O_4$.	Found.
C	62.60	62.38
H	9.56	9.18

Experiments with β-Ethoxypropiophenone.

Preparation.—β-Ethoxypropiophenone has been obtained as a by-product in the preparation of vinylphenyl ketone from dibrompropiophenone. My material was made by the same reaction but by a different procedure since it was necessary to have a product entirely free from unsaturated ketone. Solid dibrom ketone was added in small portions to an alcohol-water solution of potassium iodide. After boiling for two hours the mixture was cooled and poured into an excess of sodium thiosulphate. Steam was passed through the solution, the distillate extracted with ether and the ethereal solution dried with fused sodium sulphate. By removal of the ether and distillation under diminished pressure, 12 grams of β-ethoxypropiophenone were obtained from 33 grams of di-

brompropiophenone. A test with bromine showed that the product contained no vinylphenyl ketone.

Reaction with Phenylmagnesium Bromide.

Ethoxyethyldiphenylcarbinol, $C_2H_5OCH_2CH_2C(C_6H_5)_2OH$. — The magnesium derivative, formed when the ketone was allowed to react with phenylmagnesium bromide, was decomposed in the usual way and the liquid product distilled under diminished pressure. On cooling, the fraction boiling at 207° (21 mm.) deposited firm, white plates which were soluble in ether, and methyl and ethyl alcohol, and after two recrystallizations from low-boiling ligroin melted at 78°. From 32 grams of ketone 30 grams of product were obtained.

Analysis:

0.1578 gram substance gave 0.4611 gram CO_2 and 0.1061 gram H_2O.

	Calculated for $C_{17}H_{20}O_2$.	Found.
C	79.68	79.69
H	7.81	7.47

This substance was shown to be a hydroxyl compound by the Grignard reaction; with ethylmagnesium bromide, ethane was evolved and the original material was regained after decomposition of the magnesium derivative.

An attempt was made to eliminate one molecule of water from ethoxyethyldiphenylcarbinol but the tertiary alcohol was recovered unchanged after being boiled for three hours with excess of acetic anhydride.

Reaction with Ethylmagnesium Bromide.

Ethylethoxyethylphenylcarbinol, $C_2H_5OCH_2CH_2C(C_2H_5)(C_6H_5)OH$. —The product obtained from the reaction between ethoxypropiophenone and ethylmagnesium bromide was a colorless, mobile

liquid boiling at 151° (24 mm.). From 33 grams of ketone 28 grams of the product resulted.

Analysis:

0.1700 gram substance gave 0.4700 gram CO_2 and 0.1453 gram H_2O.

	Calculated for $C_{13}H_{20}O_2$.	Found.
C	75.00	75.40
H	9.61	9.49

This substance was likewise shown to be a hydroxyl compound by the Grignard reaction.

Experiments with β-Ethoxybenzalacetophenone.

Preparation.—For the preparation of the large quantities of β-ethoxybenzalacetophenone needed in this work, the methods recommended by Wislicenus[1] and by Ruhemann and Watson[2] were tried, but neither was found satisfactory. The process by which this ketone is formed from dibrombenzalacetophenone is more involved than assumed by these investigators, for Wislicenus regarded the substance as an isomer of dibenzoylmethane and Ruhemann and Watson thought that it could be formed from the corresponding β-brom ketone by direct replacement of bromine with the ethoxyl group.

The reactions by which β-ethoxybenzalacetophenone is formed may be represented by the following equations:

I. $C_6H_5CHBrCHBrCOC_6H_5 - HBr \longrightarrow C_6H_5CH : CBrCOC_6H_5$;

II. $C_6H_5CH : CBrCOC_6H_5 + NaOC_2H_5 \longrightarrow C_6H_5C(OC_2H_5) : CHCOC_6H_5$.

As the first step certainly consists in elimination of hydrobromic acid the procedure of Wislicenus, in which α-brombenzalacetophenone is first made and subsequently transformed in accordance with equation II, seemed the most promising.

It is easy to remove one molecule of hydrobromic acid,

[1] Ann. Chem. (Liebig), **308**, 219.

[2] J. Chem. Soc., **88**, 456.

quantitatively, by boiling the dibrombenzalacetophenone with potassium acetate. Though the resulting α-brom ketone is a solid, the product obtained by distillation under diminished pressure frequently remains liquid for weeks. It can be identified readily, however, by the solid pyrazol formed by treating the ketone with semicarbazide hydrochloride and potassium acetate in the usual way. The solid separates only from concentrated solutions but it is easily purified by recrystallization from alcohol, from which it is deposited in needles melting at 199°–200°.

Analysis:

I. 0.1549 gram substance gave 0.4620 gram CO_2 and 0.0781 gram H_2O.

II. 0.1606 gram substance gave 0.4788 gram CO_2 and 0.0805 gram H_2O.

	Calculated for $C_{15}H_{12}N_2$	Found. I.	II.
C	81.82	81.34	81.30
H	5.45	5.60	5.56

This is the same 3,5-diphenylpyrazol previously obtained by Knorr[1] by treating dibenzoylmethane with hydrazine, and by Wislicenus[2] by treating β-ethoxybenzalacetophenone with semicarbazide. Its formation from α-brombenzalacetophenone is represented by the following equations:

$$C_6H_5CH{:}CBrCOC_6H_5 + NH_2CONHNH_2 \rightarrow C_6H_5CHCHBrCC_6H_5$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \qquad\quad ||$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad H_2NOC.N\text{———}N \quad ;$$

$$C_6H_5CHCHBrCC_6H_5 \qquad\qquad C_6H_5CHCHBrCC_6H_5 \qquad\qquad$$
$$\quad | \qquad\quad || \qquad\qquad\quad | \qquad\quad || \qquad\qquad$$
$$H_2NOC.N\text{———}N \longrightarrow HOOC.N\text{———}N \longrightarrow$$

$$C_6H_5C{:}\ CHCC_6H_5$$
$$\quad | \qquad\quad ||$$
$$HN\text{——}N \qquad + CO_2 + HBr.$$

Although it was easy to get the α-brom ketone, this method of procedure was abandoned because the yield of β-ethoxyl compound was poor. A poor yield was likewise obtained

[1] Ber. d. chem. Ges., **36**, 116.

[2] Ann. Chem. (Liebig), **308**, 256.

when dibrombenzalacetophenone was treated with potassium hydroxide and this method had the additional disadvantage that a large quantity of absolute alcohol was needed.

I found that I could readily get a fair yield of β-ethoxybenzalacetophenone by starting with the dibrom ketone and substituting sodium alcoholate for potassium hydroxide. My method of procedure was as follows: Twenty-six grams of metallic sodium were added to 400 cc. of absolute alcohol. The flask was connected with an inverted condenser and the solution heated to boiling; 210 grams of solid dibrombenzalacetophenone were then added gradually, and the boiling continued for half an hour. The sodium bromide was filtered with suction and washed free of organic material with alcohol. The liquid resulting after removal of the alcohol was fractioned under diminished pressure. It gave 110 grams of a blood-red, viscous product boiling at 217° (18 mm.). On dilution with an equal volume of alcohol the liquid deposited solid β-ethoxybenzalacetophenone, which was purified by recrystallization from alcohol. Yield, 70 grams. The filtrate contained a mixture of unsaturated ketone and dibenzoylmethane which was very difficult to separate.

This method of procedure gives no clue as to the mechanism by which β-ethoxybenzalacetophenone is formed. That it has the structure assigned to it, however, was established by Ruhemann and Watson, who heated the ketone in a sealed tube with hydrochloric acid and found that decomposition took place in accordance with the following equation:

$$\begin{matrix} C_6H_5 \\ C_2H_5O \end{matrix}\!\!\diagdown\!\!\diagup C : CHCOC_6H_5 + HCl + H_2O \longrightarrow$$

$$C_6H_5COOH + CH_3COC_6H_5 + C_2H_5Cl.$$

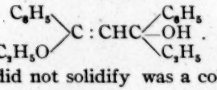
Reaction with Ethylmagnesium Bromide.—Solid β-ethoxybenzalacetophenone was allowed to react with ethylmagnesium bromide in the usual way. On each addition of ketone a green solid separated, which redissolved immediately and colored the whole solution a brilliant green. The magnesium derivative was decomposed at once with iced hydrochloric acid and the solid product which appeared in the ethereal

layer filtered with suction. On slow evaporation of the ether one gram of another solid separated. This crystallized from alcohol in fine white needles, readily soluble in methyl alcohol, acetone, chloroform and ether, and melting at 60°.5.

Analysis:

0.1563 gram substance gave 0.4595 gram CO_2 and 0.0987 gram H_2O.

	Calculated for $C_{19}H_{22}O_2$.	Found.
C	80.85	80.17
H	7.80	7.02

This substance is ethoxydiphenylethylallyl alcohol,  . The portion of the product which did not solidify was a colorless, mobile liquid distilling at 96° (18 mm.). From 20 grams of ketone there resulted 10 grams of this substance.

Analysis:

0.1569 gram substance gave 0.4654 gram CO_2 and 0.1022 gram H_2O.

	Calculated for $C_{19}H_{22}O_2$.	Found.
C	80.85	80.89
H	7.80	7.23

On treatment of the liquid with semicarbazide hydrochloride and potassium acetate, a solid was deposited in fine, white needles, which, after two recrystallizations from alcohol, melted at 161°.

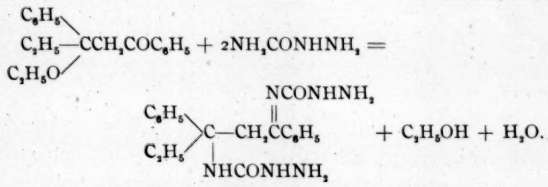
Analysis:

I. 0.1779 gram substance gave 0.4043 gram CO_2 and 0.1017 gram H_2O.

II. 0.1700 gram substance gave 0.3866 gram CO_2 and 0.0995 gram H_2O.

	Calculated for $C_{19}H_{23}O_2N_3$.	Found. I.	Found. II.
C	61.95	61.98	62.02
H	6.52	6.35	6.50

This reaction showed that the liquid product is a ketone; it is ethoxyphenylethylpropiophenone, formed by 1,4-addition of ethylmagnesium bromide to β-ethoxybenzalacetophenone. By the action of two molecules of semicarbazide the semicarbazidesemicarbazone of ethoxyphenylethylpropiophenone was formed, as represented by the following equation:



When the solid product which first appeared after decomposition of the magnesium derivative was digested with chloroform, a very small quantity of a powdery, white substance separated; this, however, was not studied because its extreme insolubility in all ordinary solvents made it difficult to purify. The chloroform solution contained two products, which were separated by fractional crystallization from a mixture of alcohol and chloroform; one formed white needles melting at 205°, the other yellow needles melting at 185°. In solution the white crystals change into the yellow crystals. Combustions and molecular weight determinations indicated that they may be represented by the formula $C_{34}H_{32}O_3$.

Analysis:

I. 0.1492 gram substance (235°) gave 0.4563 gram CO_2 and 0.0795 gram H_2O.

II. 0.1672 gram substance (185°) gave 0.5113 gram CO_2 and 0.0801 gram H_2O.

	Calculated for $C_{34}H_{32}O_3$.	Found. I.	Found. II.
C	83.60	83.40	83.40
H	6.55	5.92	5.32

The molecular weight of the stable yellow product was determined in carbon tetrachloride (K = 48.0).

Solvent, grams.	Substance, gram.	Rise of boiling point.	Molecular weight.
95	0.5977	0.07	431
95	1.1200	0.13	435
	Calculated for $C_{34}H_{32}O_3$.		488

Since β-ethoxybenzalacetophenone has no substituent in the α position, it might be expected to give secondary reactions, and these two substances undoubtedly are secondary products. The white crystals change slowly in solution into the yellow crystals. They may be stereoisomers and may result, with elimination of alcohol, by the action of β-ethoxybenzalacetophenone on the 1,4-addition product first formed in the reaction.

Diphenylmethylethylbutadiene, $\begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}\!\!>\!C : CHC : CHCH_3$, —
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C_6H_5$

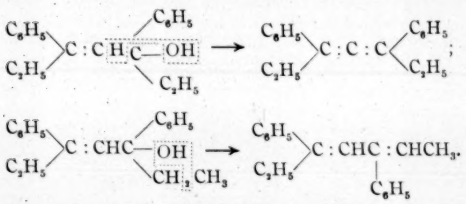
When the reaction between ethylmagnesium bromide and β-ethoxybenzalacetophenone was carried out a second time, by chance a much larger quantity of ether was used than in the first experiment. On decomposition of the brilliant green product, the same three high-melting solids previously obtained separated from the ethereal layer, but the portion left after removal of the ether was a colorless liquid boiling at 191°–195° (20 mm.).

Analysis:

0.1851 gram substance gave 0.6100 gram CO_2 and 0.1340 gram H_2O.

	Calculated for $C_{19}H_{20}$.	Found.
C	91.93	89.87
H	8.06	8.04

This analysis indicated an impure hydrocarbon and a test with hydroxylamine showed the presence of ketone. Accordingly the liquid was boiled with hydroxylamine hydrochloride and sodium hydroxide; analysis of the product obtained after this reaction again indicated a hydrocarbon contaminated by some oxygen compound, but it was impossible to separate a pure product by distillation. This substance could be either a butadiene or an allene derivative:



If the substance is diethyldiphenylallene it would be expected to give reactions analogous to those of tetraphenylallene[1] which Vorländer found to be comparatively unreactive. Tetraphenylallene does not decolorize bromine in a freezing mixture nor does it reduce potassium permanganate; the product obtained, however, gives both of these reactions. The liquid was treated with an acetone solution of potassium permanganate, which was reduced rapidly in the cold; the oxidation products isolated were benzoic acid and ethylphenyl ketone. The ketone was identified by its semicarbazone,

$$C_6H_5C(:NNHCONH_2)C_2H_5,$$

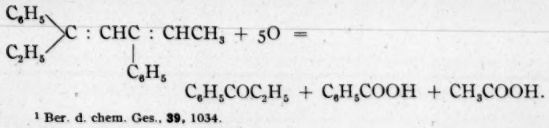
which crystallizes from alcohol in fine white needles melting at 176°.

Analysis:

0.1523 gram substance gave 0.3493 gram CO_2 and 0.0918 gram H_2O.

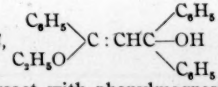
	Calculated for $C_{10}H_{13}ON_3$.	Found.
C	62.82	62.55
H	6.80	6.69

The oxidation reaction, represented by the following equation, establishes beyond doubt that the liquid is a butadiene derivative:



[1] Ber. d. chem. Ges., **39**, 1034.

Reaction with Phenylmagnesium Bromide.—Solid β-ethoxybenzalacetophenone was added to phenylmagnesium bromide in the presence of a large quantity of ether, as in the second reaction with ethylmagnesium bromide. The Grignard product was decomposed in the usual way and the solid which appeared at once in the ethereal layer was precipitated by addition of low-boiling ligroin. The white crystalline product, which has the melting point, 139°, of tetraphenylallyl alcohol,[1] was identified by treatment with acetic anhydride, which transformed it quantitatively into tetraphenylallene, melting at 164°–165°. The residue left after the removal of the solvent also contained a small quantity of the allene hydrocarbon. Tetraphenylallene was likewise obtained by Vorländer on decomposing the product formed when phenylbenzalacetophenone was treated with phenylmagnesium bromide.

Ethoxytriphenylallyl Alcohol,  .—When the ketone was allowed to react with phenylmagnesium bromide in the presence of the usual quantity of ether a solid was isolated in the same way as in the last experiment; it crystallized from alcohol in fine, white needles, soluble in acetone, chloroform, ether and methyl alcohol and melting at 120°.5.

Analysis:

0.1490 gram substance gave 0.4566 gram CO_2 and 0.0812 gram H_2O.

	Calculated for $C_{29}H_{24}O_2$.	Found.
C	83.63	83.57
H	6.66	6.05

Reaction with ethylmagnesium bromide showed that this substance is a hydroxyl compound. From 20 grams of ketone 15 grams of ethoxytriphenylallyl alcohol were obtained, but the remainder of the product could not be made to crystallize. As this tertiary alcohol might be expected to lose water, like tetraphenylallyl alcohol, and form an interesting

[1] Ber. d. chem. Ges., **39**, 1026.

allene derivative, both the carefully purified solid and the residue left after removal of the solvents were treated with acetic anhydride. The sole product identified in each case was benzophenone.

BRYN MAWR COLLEGE,
May, 1910.

A COMPARISON OF CERTAIN ACIDS CONTAINING A CONJUGATED SYSTEM OF DOUBLE LINKAGES.[1]

BY ANNIE LOUISE MACLEOD.

The substituted cinnamylidenacetic acids are of particular interest because they contain the juxtaposed double linkages to which Thiele has given the name of a "conjugated system." Since the character of substances is changed by the introduction of various groups into the α position to the carboxyl it is possible to use these substituted acids for the purpose of studying the influence of substituents upon the mode of addition to such a conjugated system.

Of the α-substituted cinnamylidene acids only two have been investigated with any degree of thoroughness, cinnamylidenemalonic acid (I), and α-phenylcinnamylidenacetic acid (II). For comparison with these I selected α-methylcinnamylidenacetic acid (III), in which the substituent is more positive, and α-cyancinnamylidenacetic acid (IV), in which the substituent is more negative than in either of the two acids above mentioned.

I. $C_6H_5.CH : CH.CH : C(COOH)_2$;

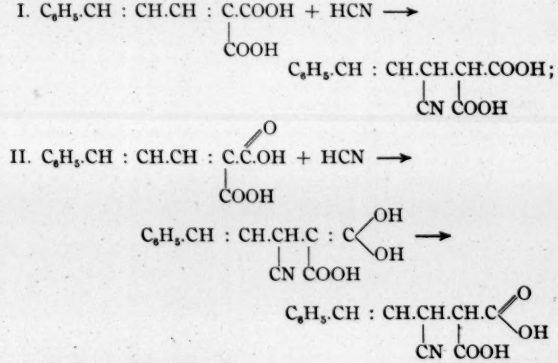
II. $C_6H_5.CH : CH.CH : C(C_6H_5).COOH$;

III. $C_6H_5.CH : CH.CH : C(CH_3).COOH$;

IV. $C_6H_5.CH : CH.CH : C(CN).COOH$.

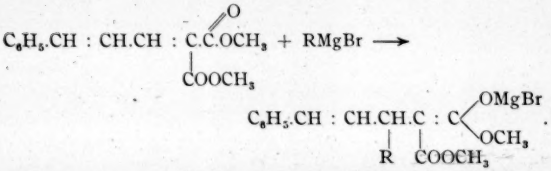
[1] Thesis offered in partial fulfilment of the requirements for the degree of Ph.D. at McGill University.

In the case of cinnamylidenemalonic acid a number of addition reactions have been studied with care. Thiele and Meisenheimer[1] found that when the methyl ester of this acid is treated with potassium cyanide and the resulting compound is hydrolyzed the product is a dicarboxylic acid with the second carboxyl in the β position. From this they inferred that the potassium cyanide reaction led to addition of hydrocyanic acid in the 1,2 position, the cyanogen group going to the β carbon atom. The addition of acid sulphites takes place in an analogous manner, the sulphoxyl group going into the β position.[2] Hinrichsen assumes a similar constitution for the products from the reactions with hydrobromic acid and with sodium alcoholate.[3] These results have been interpreted by Hinrichsen as representing direct 1,2-addition, but a different explanation is possible, namely, that in each of these cases the reaction consists primarily in 1,4-addition to the system —C : C.C : O, the hydrogen going to the oxygen of the carbonyl group, from which it subsequently shifts to the adjoining carbon atom. These two views are represented by the following scheme:

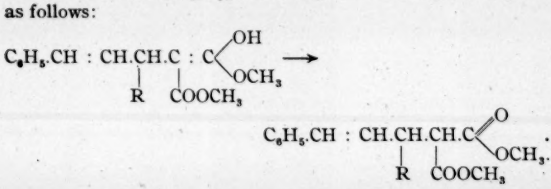


[1] Ann. Chem. (Liebig), **306**, 247.
[2] Kohler: This Journal, **31**, 234.
[3] Ann. Chem. (Liebig), **336**, 200.

It is impossible to prove either view to be the correct one in the case under discussion, but the latter would seem the more probable if we reason from the analogous reactions with alkylmagnesium compounds. It has been shown by Reimer[1] that when methyl cinnamylidenemalonate is treated with a Grignard reagent, the magnesium goes to the carbonyl oxygen while the alkyl group goes to the carbon atom which stands in position 4 with regard to this oxygen:

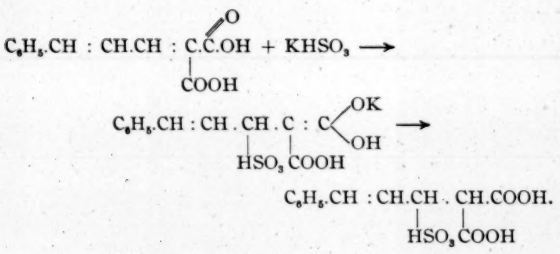


After decomposition, however, the hydrogen by which the magnesium has been replaced is found to occupy the α position to the carboxyl group, rearrangement having taken place as follows:



As this is the only addition reaction which can be followed step by step, and since in this case a reaction which apparently consists in 1,2-addition to the system C : C.C : C is found actually to consist in 1,4-addition to the system C : C.C : O, it seems justifiable, in the absence of any proof to the contrary, to assume the existence of such an intermediate compound in other similar cases, such as the reaction between cinnamylidenemalonic acid and acid potassium sulphite:

[1] This Journal, **38**, 227.



Under the influence of sunlight cinnamylidenemalonic acid forms a tetramethylene derivative. In this reaction it is the γ,δ linkage which is involved,[1] as is also the case in the reaction with bromine.[2]

Hinrichsen and Lohse[3] prepared the dibromide of α-cyan-cinnamylidenacetic acid, and found that with this acid also the bromine goes into the 3,4 position with regard to the carboxyl. A similar constitution has been proved for the dibromide of α-phenylcinnamylidenacetic acid.[4] As the difference between the mode of addition of hydrocyanic acid, acid sulphites, and similar reagents, and that of hydrogen to cinnamylidenemalonic ester is attributed by Hinrichsen to the fact that in the latter case only the molecule is symmetrical, he attempted to prepare addition products of α-cyan- and α-phenylcinnamylidenacetic acids with unsymmetrical reagents, but found that either addition did not take place at all or the product was so unstable that it could not be isolated.

Reimer and Reynolds[5] found that methyl α-phenylcinnamylidenacetate reacts, though not readily, with magnesium compounds, the product obtained consisting of 87 per cent. ketone formed by replacement of the methoxyl group and addition

[1] Rüber: Ber. d. chem. Ges., **35**, 2411.
[2] Hinrichsen: Ann. Chem. (Liebig), **336**, 200.
[3] Ann. Chem. (Liebig), **336**, 327.
[4] Hinrichsen: *Loc. cit.*
[5] This Journal, **40**, 428.

of a second molecule of the magnesium compound in the 1,4 position to the resulting ketone:

$$C_6H_5.CH : CH.CH : \underset{\displaystyle C_6H_5}{\overset{|}{C}}.COOR + 2C_6H_5MgBr \longrightarrow$$

$$C_6H_5.CH : CH.\underset{\displaystyle C_6H_5}{\overset{|}{CH}}.C : C\begin{matrix}OMgBr \\ C_6H_5\end{matrix} + MgORBr.$$

According to these investigators the difference between the behavior of this ester and that of α-phenylbenzylidenacetate,

$$C_6H_5CH : \underset{\displaystyle C_6H_5}{\overset{|}{C}}.COOR,$$

which gives only 1,4-addition product with no replacement of the alkoxyl group,[1] is to be attributed to the spatial arrangement of the molecule.

I have found that the ethyl ester of α-cyancinnamylidenacetic acid reacts readily with both aliphatic and aromatic magnesium compounds, giving a quantitative yield of the 1,4-addition product. The course of the reaction is as follows:

$$C_6H_5.CH : CH.CH : \underset{\displaystyle CN}{\overset{|}{C}}.\underset{\displaystyle OC_2H_5}{\overset{|}{C}} : O + RMgBr \longrightarrow$$

$$C_6H_5.CH : CH.\underset{\displaystyle R}{\overset{|}{CH}}.\underset{\displaystyle CN}{\overset{|}{C}} : \underset{\displaystyle OC_2H_5}{\overset{|}{C}}.OMgBr.$$

When this compound is decomposed by water the resulting enol changes to the corresponding ketonic form, so that the final product is the ester

$$C_6H_5.CH : CH.\underset{\displaystyle R}{\overset{|}{CH}}.\underset{\displaystyle CN}{\overset{|}{CH}}.COOC_2H_5.$$

That the magnesium is in combination with carbon, as has been assumed above, and not with the nitrogen of the cyan-

[1] Kohler and Heritage: THIS JOURNAL, **45**, 153.

ogen group, as in the reaction with ethyl cyanacetate,[1] follows from the fact that the substance gave no reaction with excess of alkyl halide. Earlier work[2] has shown that 1,4-addition products that have magnesium in combination with nitrogen react with halogen alkyls, giving *C*-alkyl derivatives, while the magnesium derivatives obtained from esters and ketones do not react at all with simple halogen alkyls. The reaction of α-cyancinnamylidenacetic ester is therefore similar in every respect to that between α-cyancinnamic ester and organic magnesium compounds.[3]

As a rule, the magnesium derivatives formed by 1,4-addition behave towards acid chlorides like the metallic derivatives of β-ketonic esters and diketones; the magnesium halide residue is replaced by an acyl group, the product being an *O*-acyl derivative. The only exception heretofore noted is in the case of the magnesium compound obtained from α-cyancinnamic acid,[4] where the acyl group replaces the diphenylmethyl group, giving the magnesium derivative of a β-ketonic ester, and diphenylchlormethane, which may subsequently react with another molecule of the magnesium compound. A precisely similar reaction takes place with the magnesium derivative of α-cyancinnamylidenacetic acid:

$$2C_6H_5.CH : CH.CH(R).C(CN) : C(OC_2H_5).OMgBr + 2CH_3COCl \longrightarrow$$

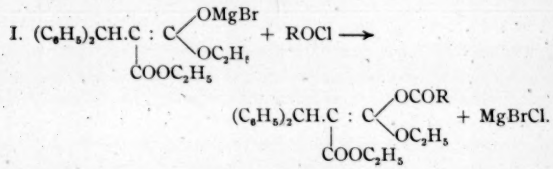
$$2C_6H_5.CH : CH.CH(R).Cl + (CH_3.CO.C(CN) : C(OC_2H_5).O)_2Mg + MgBr_2;$$

$$C_6H_5.CH : CH.CH(R).C(CN) : C(OC_2H_5).OMgBr + C_6H_5.CH : CH.CH(R).Cl \longrightarrow$$

$$C_6H_5.CH : CH.CH(R).C(CN) : C(OC_2H_5).O.CH(R).CH : CH.C_6H_5 + MgBrCl.$$

[1] Blaise: Compt. rend., **139**, 674.
[2] Kohler: This Journal, **35**, 386.
[3] Kohler and Reimer: *Ibid.*, **33**, 333.
[4] Kohler and Reimer: *Loc. cit.*

This remarkable reaction depends upon the presence of a cyanogen and an ester group attached to the same carbon atom, as is evident from the fact that it does not take place with the magnesium derivatives of either benzalmalonic ester[1] or α-phenylcinnamonitrile,[2] the respective reactions in these cases being as follows:



II. $C_6H_5.CH.C : C : NMgBr + RCOCl \longrightarrow$ $C_6H_5.CH.C(COR).CN + MgBrCl.$

When exposed to sunlight, α-cyan-, α-phenyl-, and α-methyl-cinnamylidenacetic acids are all decolorized. In the case of the two first mentioned the reaction is extremely slow, so that it was not possible to isolate a definite product. When the α-cyan acid in a very finely divided state is suspended in water containing hydrochloric acid and exposed to strong sunlight it slowly goes into solution, probably undergoing hydrolysis to the acid amide. The sunlight evidently acts as a catalyst in this reaction, as a similar suspension was kept for months in the dark without any appearance of dissolving. The α-methyl acid is apparently acted upon by sunlight more rapidly than any other unsaturated acid heretofore observed, the reaction being complete in four days. The product is a tetramethylene derivative corresponding to that obtained from cinnamylidenemalonic acid:

[1] Kohler: THIS JOURNAL, **34**, 132.
[2] *Ibid.*, **35**, 386.

$$2C_6H_5.CH : CH.CH : C(CH_3).COOH \longrightarrow$$

$$C_6H_5 : CH.CH.CH : C(CH_3).COOH.$$
$$COOH.C(CH_3) : CH.CH.CH.C_6H_5$$

The dimeric acid, like the corresponding substance obtained from cinnamylidenemalonic acid, dissolves in cold concentrated sulphuric acid, giving a pale yellow solution. If the acid is immediately reprecipitated with water it can be recovered unchanged, but if it is left standing overnight in sulphuric acid solution the double molecule is broken down and the monomolecular form is obtained on precipitation. A similar disruption of the double molecule takes place when it is distilled under diminished pressure. This is in accord with Liebermann's observation[1] that α-truxillic acid changes into cinnamic acid on distillation.

Both α-cyan- and α-methylcinnamylidenacetic acids readily react with acid potassium sulphite, giving colorless addition products. These products could not be isolated, however, as they break down, slowly in the cold but rapidly on heating, into their components. The fact that cinnamylidenemalonic acid alone of the α-substituted cinnamylidene acids gives addition products with acid sulphites which can be isolated probably depends not so much on any greater stability of these products so much as on the fact that they contain a second carboxyl group, by means of which more favorable manipulation is possible.

With bromine α-methylcinnamylidenacetic acid gives either a di- or tetrabromide according to the conditions of the reaction.

EXPERIMENTAL.

Experiments with α-Methylcinnamylidenacetic Acid, $C_6H_5.CH : CH.CH : C(CH_3).COOH.$

Preparation.—The method first adopted was that described

[1] Ber. d. chem. Ges., **22**, 124.

by Perkin,[1] namely, by heating cinnamic aldehyde, propionic anhydride, and sodium propionate to 160° in a flask fitted with an air condenser. The yield of crude acid obtained in this way amounted to 84 per cent. of the calculated quantity. In later experiments the propionic anhydride was replaced by propionyl chloride and sodium propionate in the proportions necessary for its formation. A mixture of 58 grams sodium propionate and 42 grams cinnamic aldehyde was heated to 160° and 40 grams propionyl chloride added through a dropping funnel at such a rate that the addition occupied from one to two hours. This method gives a somewhat poorer yield (58 per cent. of the calculated quantity), but seems on the whole preferable to that first described on account of the difficulty of obtaining pure propionic anhydride.

The acid obtained by either of these methods is pale yellow, but becomes white on exposure to the light. Perkin makes no mention of this fact, nor does he describe the color of his acid, merely stating that the crystals became opaque on standing. Both forms, and a mixture of the two, have the same melting point, beginning to soften at 158° and melting at 160°–161°.

Analysis:

Yellow acid—0.1680 gram substance gave 0.4718 gram CO_2 and 0.0944 gram H_2O.

	Calculated for $C_{12}H_{12}O_2$.	Found.
C	76.59	76.59
H	6.38	6.24

White acid—0.1618 gram substance gave 0.4543 gram CO_2 and 0.0940 gram H_2O.

	Calculated for $C_{12}H_{12}O_2$.	Found.
C	76.59	76.69
H	6.38	6.45

It was of interest to determine whether we have here a case of isomerism, for which there are several possibilities in the structure of this acid, or whether the yellow color is due to

[1] J. Chem. Soc., **31**, 406.

some impurity. The following experiments were undertaken in order to determine this point.

Crystallization.—The yellow acid separates from alcoholic solution in thick prisms, the white form in flat, leaflike plates. Neither the melting point nor the crystalline form is affected by repeated crystallization. The yellow color becomes slightly paler, which may be due either to gradual dilution of an impurity present, or to partial transformation of one isomer into another during the process of recrystallization.

Crystallization of Mixed Acids.—Equal quantities of yellow and of white acids, each specimen having been carefully purified by recrystallization, were ground up together in a mortar and dissolved in sufficient alcohol to make a fairly dilute solution. Into the cold solution a yellow and a white crystal were introduced at opposite sides of the beaker, and the whole left to crystallize slowly in the dark. Under these conditions the crystals which separated out were of a uniform pale yellow color, and all in the thick prisms characteristic of the yellow acid. At the end of the experiment the original yellow and white crystals each formed the core of a crystalline mass, from which they could readily be distinguished by the color, which was paler in one case, deeper in the other. It is evident, therefore, that if there are two isomeric acids they are capable of crystallizing together in mixed crystals, a phenomenon which is unusual though not unknown in the case of stereoisomers. Klingemann[1] has observed that the two forms of benzylidenedesoxybenzoin behave similarly.

Purification through Sodium Salt.—If the yellow acid be dissolved in sodium carbonate solution the salt which crystallizes out is colorless. This salt was ground finely, extracted with ether for eight hours in a Soxhlet apparatus, and recrystallized from water, in which it is very soluble and from which it separates in colorless shining plates. The acid obtained from this salt by precipitating with hydrochloric acid and recrystallizing from alcohol was lemon-yellow. It follows that if the yellow color is due to an impurity this impurity must be an acid substance, since it imparts no color to the

[1] Ann. Chem. (Liebig), **275**, 60.

sodium salt and cannot be extracted from it by organic solvents. No variation could be detected in the color of the resulting acid either by use of a very weak acid, such as carbonic acid, for precipitating from a solution of the sodium salt, or by fractional precipitation by hydrochloric acid.

Esterification.—The acid is readily esterified, the reaction being complete on boiling for three hours with a three per cent. solution of hydrochloric acid in methyl alcohol. The products from the yellow and white forms are identical, a well-defined crystalline compound being obtained in each case. This is easily purified by recrystallization from methyl alcohol, in which it is readily soluble, and from which it separates in colorless needles melting at 87°.

Analysis:

0.1717 gram substance gave 0.4855 gram CO_2 and 0.1038 gram H_2O.

	Calculated for $C_{13}H_{14}O_2$.	Found.
C	77.22	77.11
H	6.93	6.75

Molecular weight:

Ether.	Substance.	Difference in boiling point.	Molecular weight.
58.948	0.2010	0.0375	196
	0.4098	0.0700	214
	0.5502	0.0950	212

Calculated for $C_{13}H_{14}O_2$, 202. Average found, 207

On treating with alcoholic potassium hydroxide the potassium salt separated as small plates on standing at room temperature for a short time, and this, on acidifying, gave a pure white acid which crystallized from alcohol in the characteristic leaflike plates. When the hydrolysis is carried out by boiling with aqueous potassium hydroxide the acid obtained is yellow.

Several cases are known in which esterification of stereoisomeric acids by boiling with three per cent. hydrochloric acid in alcohol results in the formation of the ester corresponding to one form only. Thus maleic acid treated in this manner gives ethyl fumarate. Similarly, β-bromcinnamic acid, under the same conditions, gives the ester of α-bromcinnamic

acid.[1] Anschütz[2] has shown that in both cases this is due to the transforming influence of the hydrochloric acid and that esterification through the silver salt with alkyl iodide gives the normal product. Accordingly, the silver salts of both the yellow and the white forms were prepared and treated with methyl iodide. The only product obtained was the ester melting at 87°.

When the yellow acid, in cold alcoholic solution, was treated with an amount of sodium amalgam sufficient to neutralize only about 4 per cent. of the acid present the yellow color disappeared, leaving the colorless acid, which crystallized from the alcoholic solution. It follows, therefore, that the substance to which the yellow color is due is present only in small amount. Whether this substance is an isomeric acid or not cannot be proved without further work, but in any case it is evident from the results described that its presence does not affect the reactions which form the specific subject of this investigation. The following experiments were carried out with yellow acid obtained by recrystallizing the crude product until it gave a constant melting point of 160°.

In the course of later experiments it was found that this acid could be more advantageously prepared by making use of the reaction between cinnamic aldehyde and α-brompropionic ester in the presence of zinc. For this purpose, 21 grams of cinnamic aldehyde, 32.5 grams brompropionic ester, and 13 grams zinc in 100 cc. dry benzene were heated for an hour and a half on the water bath. At the end of this time the solution was poured into dilute hydrochloric acid and extracted with ether. After evaporating the ether the product left was a yellow oil which would not solidify. This was undoubtedly the hydroxy ester formed according to the scheme:

$$C_6H_5.CH : CH.CHO + \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}Br.COOCH_3 + Zn \xrightarrow{+H_2O}$$

$$C_6H_5.CH : CH.\underset{\displaystyle OH}{\overset{\displaystyle |}{CH}}.\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}.COOCH_3 + ZnBrOH.$$

[1] Barisch: J. prakt. Chem., **20**, 182.
[2] Ber. d. chem. Ges., **13**, 2282; **20**, 1382.

On distillation under diminished pressure this ester loses water, giving the ester of α-methylcinnamylidenacetic acid:

$$C_6H_5.CH : CH.\underset{OH}{CH}.\underset{CH_3}{CH}.COOCH_3 \longrightarrow C_6H_5.CH : CH.CH : \underset{CH_3}{C}.COOCH_3.$$

A yield of from 80 to 90 per cent. of the calculated amount of this ester is obtained in this way.

Effect of Light.—In order to obtain the acid in the most suitable condition for exposure, 10 grams were dissolved in sodium carbonate solution and made up to about two liters in a large flask. Dilute hydrochloric acid was added slowly until the whole amounted to about four liters. After exposure to bright sunlight for half an hour the suspended acid appeared quite white, but this change was probably only superficial, as the crystals obtained after filtering, drying, and recrystallizing were yellow. After exposure to sunlight for eight hours, with occasional shaking, the acid, after filtering and drying, separated from alcohol in thin plates which were perfectly colorless. There was no appreciable change in melting point after exposure for this length of time.

When the exposure was continued for about four days in direct sunlight the suspended acid was found to have undergone further change. The product was difficultly soluble in alcohol and crystallized from it in small white prisms melting at 253°–254°.

Analysis:

0.1243 gram substance gave 0.3487 gram CO_2 and 0.0723 gram H_2O.

	Calculated for $C_{24}H_{24}O_4$.	Found.
C	76.59	76.35
H	6.38	6.51

Oxidation.—The constitution of this high-melting product was determined by oxidation. For this purpose 13.5 grams

of acid, which had been exposed to sunlight for over a week, was dissolved in slight excess of sodium carbonate solution and 53 grams of powdered potassium permanganate added. After standing overnight the oxides of manganese were filtered off and the filtrate acidified with hydrochloric acid. An acid separated, which, after several recrystallizations, first from 50 per cent. alcohol and finally from benzene and ligroin, melted at 174°, the melting point of α-truxillic acid.

Identification with this acid was completed by preparing the dimethyl ester. On saturating a solution of the acid in methyl alcohol with hydrochloric acid a crystalline ester separated which melted at 174°.

Analysis:

0.2288 gram substance gave 0.6205 gram CO_2 and 0.1222 gram H_2O.

	Calculated for $C_{20}H_{20}O_4$.	Found.
C	74.07	73.98
H	6.17	5.99

The filtrate from the α-truxillic acid, on evaporation, deposited benzoic acid, which was recrystallized and identified by its melting point. The filtrate from this was extracted with ether, neutralized with ammonia, and treated with calcium chloride solution. A fine white precipitate separated, which was found to be calcium oxalate.

The products of oxidation are therefore α-truxillic acid, benzoic acid, and oxalic acid, from which it is evident that the high-melting acid contains a tetramethylene ring. It is a compound analogous to that formed by cinnamylidenemalonic acid in sunlight.[1]

Diphenyltetramethylenebismethylenepropionic Acid,

$$\begin{array}{l} C_6H_5.CH.CH.CH:C.COOH.\text{—This is a colorless acid,} \\ \quad\quad\quad\

ble in glacial acetic acid; insoluble in choroform, benzene, and ether.

Methyl Diphenyltetramethylenebismethylenepropionate.—When the acid is boiled with a three per cent. solution of hydrochloric acid in methyl alcohol it gives an ester which crystallizes well from methyl alcohol and melts at 126°.5–127°.

Analysis:

0.1441 gram substance gave 0.4076 gram CO_2 and 0.0888 gram H_2O.

	Calculated for $C_{26}H_{28}O_4$.	Found.
C	77.22	77.14
H	6.93	6.84

On distilling under a pressure of 32 mm. the acid boiled constantly at 238°, the product being a clear yellow substance which, on recrystallization, proved to be pure α-methylcinnamylidenacetic acid, melting at 160°–161°.

Bromine Addition Product.—When diphenyltetramethylenebismethylenepropionic acid was treated with bromine a solid product was obtained which, on analysis, appeared to be a mixture of dibromide and tetrabromide. The methyl ester, on treatment with bromine in chloroform solution, gives a solid tetrabromide which can be recrystallized from chloroform, in which it is readily soluble. It separates in fine needles which melt at 200°–201°.

Analysis:

0.1830 gram substance gave 0.2891 gram CO_2 and 0.0634 gram H_2O.

	Calculated for $C_{26}H_{28}O_4Br_4$.	Found.
C	43.09	43.08
H	3.86	3.85

Addition of Bromine to Methyl α-Methylcinnamylidenacetate.—When bromine is added to a solution of the methyl ester of α-methylcinnamylidenacetic acid in carbon bisulphide which is kept cold in a freezing mixture, addition takes place very slowly. If a crystal of iodine be added the reaction is accelerated. The product is a tetrabromide, which separates as a solid on evaporating the solution. After recrystallizing,

first from alcohol and finally from a mixture of chloroform and alcohol, it is obtained in the form of very small colorless prisms, melting at 128°.

Analysis:

0.2593 gram substance gave 0.2882 gram CO_2 and 0.0627 gram H_2O.

	Calculated for $C_{13}H_{12}O_2Br_4$.	Found.
C	29 90	30.20
H	2.68	2.71

In the absence of iodine the product is a dibromide. This is formed both when the reaction mixture is cooled with ice water and kept in the dark, in which case it takes from two to three days to come to an end, and also at room temperature in the sunlight, in which case decolorization is almost instantaneous. It can be recrystallized from a mixture of ligroin and ether, from which it separates in small colorless needles melting at 81°.

Analysis:

0.1860 gram substance gave 0.2941 gram CO_2 and 0.0677 gram H_2O.

	Calculated for $C_{13}H_{14}O_2Br_2$.	Found.
C	43.09	43.12
H	3.86	4.08

When this substance is added to an alcoholic solution of potassium iodide it readily liberates iodine in the cold, a fact which indicates that the bromine atoms are attached to adjoining carbon atoms, since in all cases hitherto investigated this result has been obtained only with substances in which they are so placed. On oxidation with potassium permanganate in acetone solution, the only product obtained was benzoic acid. When a small amount of acetic acid was added to the acetone solution before oxidation, a small amount of substance was obtained which contained halogen, but which no longer liberated iodine in alcoholic potassium iodide solution. This substance is insoluble in sodium carbonate solution. It crystallizes from ether, in which it is very readily

soluble, in clusters of fine needles melting at 131°. Its constitution has not as yet been determined, owing to the difficulty of securing sufficient material for investigation. Straus[1] met with similar difficulties in attempting to determine the constitution of symmetrical diphenylbutadiene by the ordinary methods of oxidation. The only satisfactory method of attack for this and similar problems is by the use of ozone as oxidizing agent, a method which was not available for the present work.

Experiments with α-Cyancinnamylidenacetic Acid,

$$C_6H_5.CH : CH.CH : \underset{\displaystyle CN}{\underset{|}{C}}.COOH.$$

Preparation.—In preparing this acid the method followed was that of Fiquet,[2] heating equivalent quantities of cinnamic aldehyde and cyanacetic acid. The crude acid was recrystallized from alcohol. The yield obtained amounted to 68 per cent. of the calculated quantity.

Ester.—The ethyl ester was prepared both by condensation of cinnamic aldehyde with cyanacetic ester, using sodium alcoholate as a condensing agent;[3] and also directly from the acid by heating for a short time with a saturated solution of hydrochloric acid in alcohol.[4] This last method gives a quantitative yield, and may be made use of for purifying the product obtained by direct condensation, which is frequently contaminated by small quantities of the corresponding acid.

Reactions with Magnesium Compounds: Ethyl α-Cyan-β-ethyl-δ-phenylallylacetate, $C_6H_5.CH : CH.\underset{\displaystyle C_2H_5}{\underset{|}{C}}H.\underset{\displaystyle CN}{\underset{|}{C}}H.COOC_2H_5$.—

When solid ethyl α-cyancinnamylidenacetate was added slowly to an ethereal solution of ethylmagnesium bromide, in the proportion of one molecule of ester to two and a half molecules of magnesium compound, it dissolved readily, sufficient heat being evolved to keep the ether boiling during

[1] Ber. d. chem. Ges., **42**, 2866.
[2] Ann. Chim. Phys., [6] **29**, 492.
[3] Bechert: J. prakt. Chem., [2] **50**, 14.
[4] Fiquet: *Loc. cit.*

the whole time of the reaction. The product, after decomposing with hydrochloric acid, extracting wth ether, and distilling off the ether on the water bath, was a clear yellow oil which was purified by distillation under diminished pressure. The boiling point was 220° (20 mm.). A quantitative yield was obtained.

Analysis:

0.1591 gram substance gave 0.4362 gram CO_2 and 0.1111 gram H_2O.

	Calculated for $C_{18}H_{19}O_2N$.	Found.
C	74.70	74.77
H	7.39	7.79

Hydrolysis.—It was found possible to hydrolyze this ester in steps. For this purpose it was dissolved in absolute alcohol, and an equivalent amount of potassium hydroxide dissolved in the minimum quantity of water added. After standing in the cold for a short time, the potassium salt was precipitated with ether and purified by solution in the minimum quantity of aqueous alcohol and reprecipitation with ether. It was then thoroughly washed with ether, dried, and analyzed.

Analyses:

I. 0.1575 gram salt gave 0.0502 gram K_2SO_4.

II. 0.1706 gram salt gave 0.0547 gram K_2SO_4.

	Calculated for $C_{14}H_{14}O_2NK$.	Found.	
		I.	II.
K	14.60	14.28	14.36

The acid, precipitated by hydrochloric acid from an aqueous solution of the potassium salt, separated as an oil which could not be made to crystallize. It was therefore heated on the water bath with alcoholic potassium hydroxide for two days. The alcohol was then evaporated and the residue dissolved in water and acidified. An oil separated, which solidified on standing. This was filtered off, washed with water, and recrystallized from acetone, from which it crystallizes in small prisms. A qualitative test showed the presence of nitrogen.

Analysis:

0.1425 gram substance gave 0.3573 gram CO_2 and 0.0912 gram H_2O.

	Calculated for $C_{14}H_{17}O_3N$.	Found.
C	68.01	68.40
H	6.88	7.19

β-Ethyl-δ-phenylallylmalonamic acid,
$C_6H_5.CH : CH.CH(C_2H_5).CH(CONH_2).COOH$, melts at 165° and is readily soluble in acetone, alcohol, and chloroform, slightly soluble in boiling water, and very slightly soluble in ether and ligroin.

Oxidation.—For this purpose 1.3 grams of the substance were dissolved in sodium carbonate and aqueous potassium permanganate added in slight excess. After filtering off the oxides of manganese and acidifying the filtrate, the products obtained were benzoic acid (0.4 gram) and a small quantity of oil which would not solidify. The formation of benzoic acid shows that the double linkage must be in the γ,δ position to the amic acid group.

β-Ethyl-δ-phenylallylacetamide,
$C_6H_5.CH : CH.CH(C_2H_5).CH_2.CONH_2$.—When β-ethyl-δ-phenylallylmalonamic acid is heated above its melting point it loses carbon dioxide and leaves β-ethyl-δ-phenylallylacetamide. This may be recrystallized from ether, from which it separates in fine needles melting at 101°.

Analysis:

0.1134 gram substance gave 0.3198 gram CO_2 and 0.0860 gram H_2O.

	Calculated for $C_{13}H_{17}ON$.	Found.
C	76.84	76.93
H	8.37	8.48

Ethyl α-Cyan-β,δ-diphenylallylacetate,
$C_6H_5.CH : CH.CH(C_6H_5).CH(CN).COOC_2H_5$.—The reaction between α-

cyancinnamylidenacetic ester and phenylmagnesium bromide was carried out as in the corresponding experiment with ethylmagnesium bromide. In this case, however, it was necessary to keep the ethereal solution boiling on the water bath during the addition of the solid ester. The product obtained, after decomposition in the usual manner, was a yellow oil which distilled unaltered under diminished pressure. Boiling point, 263° at 18 mm.

Analysis:

0.1411 gram substance gave 0.4060 gram CO_2 and 0.0830 gram H_2O.

	Calculated for $C_{20}H_{19}O_2N$.	Found.
C	78.68	78.47
H	6.22	6.60

On oxidation with potassium permanganate the only solid product which could be obtained was benzoic acid, which was formed in the calculated quantity. The double linkage is therefore in the γ,δ position to the carbethoxyl group.

Action of Acetyl Chloride on the Magnesium Derivatives Obtained from α-Cyancinnamylidenacetic Ester.—This reaction was carried out with both the ethylmagnesium bromide and the phenylmagnesium bromide derivatives. The solid ester was added to a solution of alkylmagnesium bromide in dry ether and heated on the water bath until reaction was complete. An ethereal solution of acetyl chloride, containing one and a half molecules of acid chloride to every atom of magnesium used, was then added slowly to the boiling solution of the magnesium derivative. A white solid separated. After boiling for from three to four hours the solid, along with the ethereal solution, was poured into iced hydrochloric acid and extracted with ether. On shaking the ethereal solution with an aqueous solution of copper sulphate a green copper salt separated in small leaflike plates. This was identified as copper cyanacetacetic ester by comparing with a specimen on hand. The filtrate left after filtering off the copper salt was distilled with steam and the residue remaining in the distilling flask extracted with ether. In the reaction with

the derivative of ethylmagnesium bromide no solid product could be obtained by this treatment, but in the case of the phenylmagnesium derivative a crystalline compound separated. This was recrystallized from a mixture of chloroform and alcohol, from which it separates in the form of thick prisms. A qualitative test showed the presence of nitrogen.

Analysis:

0.1246 gram substance gave 0.3856 gram CO_2 and 0.0734 gram H_2O.

	Calculated for $C_{20}H_{21}O_3N$.	Found.
C	84.50	84.43
H	6.23	6.61

The course of the reaction is therefore as follows:

$$2C_6H_5.CH : CH.\underset{R}{CH}.\underset{CN}{C} : \underset{OC_2H_5}{C}.OMgBr + 2CH_3COCl \longrightarrow$$

$$2C_6H_5.CH : CH.\underset{R}{CH}.Cl + (CH_3.CO.\underset{CN}{C} : \underset{OC_2H_5}{CO})_2Mg + MgBr_2;$$

$$C_6H_5.CH : CH.\underset{R}{CH}.Cl + C_6H_5.CH : CH.\underset{R}{CH}.\underset{CN}{C} : \underset{OC_2H_5}{C}.OMgBr \longrightarrow$$

$$C_6H_5.CH : CH.\underset{R}{CH}.\underset{CN}{C} : \underset{OC_2H_5}{C}.O.\overset{R}{\underset{|}{C}}H.CH : CH.C_6H_5 + MgBrCl.$$

Addition of Acid Sulphites.—When α-cyancinnamylidenacetic acid is heated for a short time with an equivalent amount of acid potassium sulphite it dissolves, giving an almost colorless solution from which hydrochloric acid precipitates no acid. This proves the existence of an acid sulphite addition product. The reaction is a reversible one, however, and the solution, when acidified with hydrochloric acid and left standing in the cold, slowly turns yellow and finally deposits a yellow precipitate of α-cyancinnamylidenacetic acid. This reaction takes place more rapidly on heating, so that it was impossible to isolate the addition product.

The investigation described above was undertaken at the suggestion of Miss M. Reimer, Barnard College, to whom I wish to express my most sincere thanks. I am also greatly indebted to Dr. E. P. Kohler, Bryn Mawr College, for his kindly interest and guidance in the course of the work.

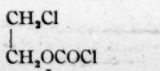
CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
May, 1910.

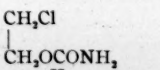
[Contributions from the Sheffield Laboratory of Yale University.]

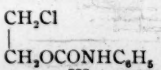
CLXXXIII.—STUDIES IN THE OXAZOLE SERIES: SYNTHESES OF ω-KETOTETRAHYDROOXAZOLES.

BY TREAT B. JOHNSON AND RALPH W. LANGLEY.

In 1885, Nemirowsky[1] observed that phosgene and chlorethyl alcohol react at 200°, giving the β-chlorethyl ester of chlorformic acid (I). He prepared, by the action of ammonia and aniline on this chloride, the corresponding urethanes, (II) and (III), and showed that the phenyl derivative (III) is converted practically quantitatively, by treatment with alkali, into the cyclic compound, N-*phenyl*-ω-*ketotetrahydrooxazole* (V). That the halogenalkyl ester of phenylcarbamic acid (III) condenses in this manner, giving a tetrahydrooxazole derivative and not an imidocarbonate (IV), was proved by the fact that the cyclic derivative underwent hydrolysis, in the presence of hydrochloric acid, giving the hydrochloride of chlorethylaniline (VI). The prototype of this series of


I.


II.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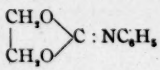
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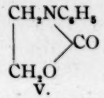
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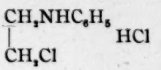
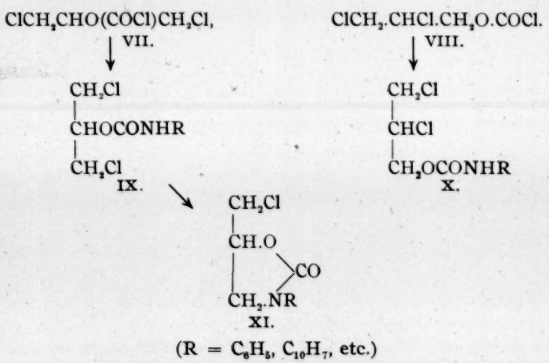

VI.

cyclic compounds, *ω-ketotetrahydrooxazole*, has been syn-

[1] J. prakt. Chem., [2] 31, 173.

thesized by Gabriel[1] by the action of silver carbonate and sodium bicarbonate on the hydrobromide of bromethylamine.

Otto[2] continued the study of the action of phosgene on chlorhydrins and investigated its behavior towards α-monochlor-α-dichlor- and β-dichlorhydrins. α-Monochlorhydrin did not react smoothly with phosgene, but from the α- and β-dichlorhydrins acid chlorides, (VII) and (VIII), were obtained, from which he prepared a series of urethanes by the action of different amines (ammonia, aniline, naphthylamines). He also investigated the action of alkali on these compounds and showed that the urethanes (IX) obtained from α-dichlorhydrin were decomposed by alkali, like the phenylurethane of chlorethyl alcohol, giving ketotetrahydrooxazoles (XI). On the other hand, all attempts to change the isomeric urethanes of β-dichlorhydrin (X) into cyclic compounds were unsuccessful. This interesting observation of Otto's has apparently received no attention. It was for the purpose of examining more carefully the behavior of phenylcarbamic-β-haloid alkyl esters towards alkali that we undertook the work described in this paper.



[1] Ber. d. chem. Ges., **21**, 566. Gabriel and Eschenbach: *Ibid.*, **24**, 2494.
[2] Diss., Rostock, 1888. J. prakt. Chem., [2] **44**, 15 (1891).

Tesmer[1] prepared the phenylurethane of glycerol by the action of phenyl isocyanate on this alcohol, but so far as the writer is aware the phenylurethanes of the haloid esters of glycero have not been prepared by this reaction. In fact, the only glycerol haloid esters of phenylcarbamic acid mentioned in the literature are apparently β,β-dichlorisopropyl phenylcarbamate (XII) and β,γ-dichlorpropyl phenylcarbamate (XIII), described by Otto.

$(ClCH_2)_2CHOCONHC_6H_5$, XII. $\quad ClCH_2.CHCl.CH_2OCONHC_6H_5$. XIII.

We have therefore investigated the action of phenyl isocyanate on all the possible dihalohydrin derivatives of glycerol containing chlorine and bromine, *viz.*:

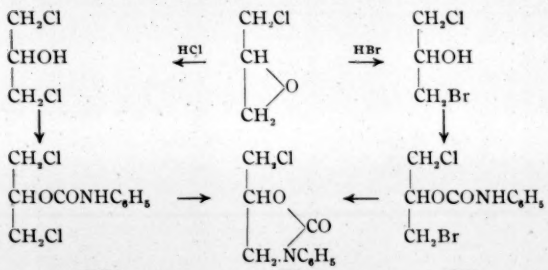
α-Dichlorhydrin, $ClCH_2CHOHCH_2Cl$.
α-Dibromhydrin, $BrCH_2CHOHCH_2Br$.
α-Chlorbromhydrin, $ClCH_2CHOHCH_2Br$.
β-Dibromhydrin, $BrCH_2.CHBrCH_2OH$.
β-Dichlorhydrin, $ClCH_2CHClCH_2OH$.
β-Chlor-γ-brompropyl alcohol, $BrCH_2CHClCH_2OH$.
β-Brom-γ-chlorpropyl alcohol, $ClCH_2CHBrCH_2OH$.

Crystalline urethanes were obtained in every case. These compounds are characterized by their great solubility in organic solvents, the β derivatives being much more soluble than the α forms. A remarkable feature of the series was the fact that every member, with the exception of the phenylurethanes of β-brom-γ-chlorpropyl alcohol and β-dibromhydrin melted at 73°. These melted at 75°–76° and 77°–79°, respectively.

α-Dichlorhydrin and β-dichlorhydrin reacted with phenyl isocyanate, giving the same urethanes, (XII) and (XIII), as were obtained by Otto by the action of aniline on the β,β-dichlorisopropyl (VII) and β,γ-dichlorpropyl (VIII) ester, respectively, of chlorformic acid. When the phenylurethane (XII) was warmed with alkali it was converted practically quantitatively into Otto's *β-chlormethyl-N-phenyl-ω-keto-tetrahydrooxazole* (XIV), melting at 104°. This same cyclic

[1] Ber. d. chem. Ges., **18**, 969.

compound was also obtained when the phenylurethane of α-chlorbromhydrin (XV) was treated with alkali under the same conditions. Since α-dichlorhydrin and α-chlorbromhydrin were prepared by addition of hydrochloric and hydrobromic acids, respectively, to epichlorhydrin, this formation of the same ketotetrahydrooxazole (XIV) from their corresponding phenylurethanes (melting at 73°) is therefore new evidence that epichlorhydrin adds the two halogen acids in a similar manner, giving secondary alcohols.

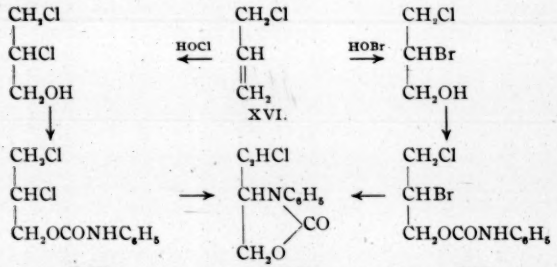


XII. XIV. XV.

While the phenylurethanes of α-dihalohydrins are easily converted into ketotetrahydrooxazoles by treatment with alkali, the corresponding urethanes of the β-dihalohydrins show great stability under the same conditions. Otto[1] states that he was unable to convert the phenylurethane of β-dichlorhydrin (XVII) into a cyclic compound. We find that this urethane undergoes an inner condensation, in presence of alkali, giving *α-chlormethyl*-N-*phenyl-ω-ketotetrahydrooxazole* (XVIII). The yield, however, was very small, since the greater proportion of the urethane underwent decomposition by the alkali. The same oxazole was also obtained when β-brom-γ-chlorpropyl phenylcarbamate (XIX) was warmed with alkali. Owing to the greater reactivity of the bromine atom in this urethane (XIX), the yield of oxazole was also

[1] *Loc. cit.*

much better than that obtained from the corresponding dichlor compound (XVII).



β-Chlor-γ-brompropyl alcohol and β-brom-γ-chlorpropyl alcohol were prepared according to Henry's[1] method by the addition of hypobromous and hypochlorous acids to allyl chloride and allyl bromide, respectively. They boil at the same temperature and have practically the same density. The only evidence so far produced to show that they are not identical is the observation by Henry[2] that when oxidized they give two isomeric acids, *viz.*, α-chlor-β-brompropionic (XX) and α-brom-β-chlorpropionic (XXI) acids:

$BrCH_2.CHCl.COOH$ (XX.) $\qquad$ $ClCH_2CHBrCOOH$ (XXI.)

Our observation, that the *ketotetrahydrooxazole* (XVIII), can be synthesized either from β-dichlorhydrin or β-brom-γ-chlorpropyl alcohol, by the action of alkali on their corresponding urethanes (XVII) and (XIX), is new evidence, therefore, that the ethylene linking in allyl halides adds hypochlorous and hypobromous acids, giving primary alcohols. In other words, the halogen atoms of the acids attach themselves to that carbon atom of the ethylene group which is joined to the least number of hydrogens. The study of the oxazole compounds is being continued in this laboratory.

[1] Ber. d. chem. Ges., **3**, 352; **7**, 757; **8**, 2288.
[2] Rec. Trav. Chim., **26**, 151.

EXPERIMENTAL PART.

β,β'-Dichlorisopropyl Phenylcarbamate, CH_2Cl | $CHO.CO.NH.C_6H_5$ | CH_2Cl.—This compound was prepared by warming at 100° α-dichlorhydrin with one molecular proportion of phenyl isocyanate. The reaction was complete within one hour and the urethane was obtained as a thick oil, which completely solidified on cooling. It is very soluble in ether, alcohol, chloroform and benzene, and insoluble in water. It was purified for analysis by crystallization from petroleum ether, and crystallized in burrs of fine needles melting at 73°. Analyses:

0.1333 gram substance gave 0.1560 gram AgCl.

Nitrogen determination (Kjeldahl):

	Calculated for $C_{10}H_{11}O_2NCl_2$.	Found.
C	28.7	28.9
N	5.65	5.93

β-Chlormethyl-N-phenyl-ω-ketotetrahydrooxazole, CH_2Cl | $CH—O$ | $CH_2.N.C_6H_5$ $>CO$.—Practically a quantitative yield of this compound was obtained as follows: Three grams of α,α-dichlorisopropyl phenylcarbamate were suspended in 20 cc. of aqueous potash (1 part alkali, 2 parts water) and heated at 100°, with shaking, for 15 minutes. Hydrochloric acid was removed by this treatment and the tetrahydrooxazole was obtained as a colorless solid insoluble in cold water. It is difficultly soluble in ligroin and ether and crystallizes from hot alcohol in slender prisms melting sharply at 104°–105° to an oil.

Nitrogen determination (Kjeldahl):

	Calculated for $C_{10}H_{10}O_2NCl$.	Found.
N	6.60	6.66

β,β'-Chlorbromisopropyl Phenylcarbamate,
CH_2Cl
|
$CHO.CONHC_6H_5$.—Symmetrical chlorbromisopropyl alcohol,
|
CH_2Br
which was prepared by addition of hydrobromic acid to epichlorhydrin, reacted at once with phenyl isocyanate, giving this carbamate. It is very soluble in alcohol and benzene and crystallizes from petroleum ether in needles melting at 73° to an oil. Analysis:

0.2223 gram substance gave 0.2546 gram AgCl + AgBr.

	Calculated for $C_{10}H_{11}O_2NClBr$.	Found.
Cl + Br	39.48	39.9
N	4.80	4.9

Behavior towards Alkali.—When the above carbamate was warmed at 100° with an aqueous solution of potassium hydroxide (1 part alkali, 2 parts water) it was converted quantitatively into *β-chlormethyl-N-phenyl-ω-ketotetrahydrooxazole*, melting at 104°. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{10}O_2NCl$.	Found. I.	Found. II.
N	6.60	6.30	6.58

β-Chlor-γ-brompropyl Phenylcarbamate,
CH_2Br
|
$CHCl$.—The β-chlor-γ-brompropyl alcohol which
|
$CH_2O.CO.NHC_6H_5$
was used for this preparation was prepared by addition of hypochlorous acid to allyl bromide. It reacted smoothly with phenyl isocyanate, when warmed on the steam bath, giving the carbamate melting at 73°. This substance is extremely soluble in alcohol and benzene and was purified by crystallization from a large volume of ligroin. Analysis:

0.2162 gram substance gave 0.2456 gram AgCl + AgBr.

	Calculated for $C_{10}H_{11}O_2NClBr$.	Found.
Cl + Br	39.48	39.58

A mixture of this carbamate and β,β'-chlorbromisopropyl phenylcarbamate (melting at 73°) melted at 60°.

β-Brom-γ-chlorpropyl Phenylcarbamate,

CH_2Cl
|
$CHBr$
|
$CH_2OCONHC_6H_5$

.—β-Brom-γ-chlorpropyl alcohol was prepared by the addition of hypobromous acid to allyl chloride. When this alcohol (4.0 grams) was warmed with phenyl isocyanate (2.7 grams) at 80° for 15 minutes, a quantitative yield of the carbamate was obtained. It was purified for analysis by recrystallization from petroleum ether and melted at 75°–76° to an oil. Analysis:

0.2169 gram substance gave 0.2494 gram AgCl + AgBr.

	Calculated for $C_{10}H_{11}O_2NClBr$.	Found.
Cl + Br	39.48	40.0

Mixtures of this carbamate with β,β'-chlorbromisopropyl phenylcarbamate (melting at 70°) and with β-chlor-γ-brompropyl phenylcarbamate (melting at 73°) melted at 62° and 60°–69°, respectively.

α-Chlormethyl-N-phenyl-ω-ketotetrahydrooxazole,

CH_2Cl
|
$CH.NC_6H_5$
| \
| CO.—One gram of β-brom-γ-chlorpropyl phenylcar-
$CH_2.O$ /

bamate was suspended in 20 cc. of water containing 10 grams of potassium hydroxide and the alkaline solution boiled for about 3 minutes. A heavy oil was obtained, insoluble in water, which completely solidified after washing with cold water. It was purified by recrystallization from ligroin and separated in burrs of needles melting at 73°–78° to a clear oil. A mixture of this substance and the original β-brom-γ-chlorpropylphenylcarbamate melted at 53°–67°. Analysis:

	Calculated for $C_{10}H_{10}O_2NCl$.	Found.	
		I.	II.
N	6.60	6.25	6.41

This same oxazole was also obtained by digestion of β,β'-dichlorpropyl phenylcarbamate with aqueous potash (1 part alkali : 2 parts water). The yield, however, was very small.

β,β-Dibromisopropyl Phenylcarbamate,

CH_2Br
|
$CHOCONHC_6H_5$.—From dibromisopropyl alcohol and phenyl
|
CH_2Br

isocyanate. It is very soluble in alcohol and ether, and insoluble in ligroin. It was purified by crystallization from ether and melted at 73°. Analyses:

0.0248 gram substance gave 0.2307 gram AgBr.

	Calculated for $C_{10}H_{11}O_2NBr_2$.	Found.
Br	47.47	47.94
N	4.20	4.15

β,γ-Dichlorpropyl Phenylcarbamate,

CH_2Cl
|
$CHCl$.—β,γ-Dichlorpropyl alcohol was prepared
|
$CH_2OCO.NHC_6H_5$

by addition of hypochlorous acid to allyl chloride. It reacted smoothly with phenyl isocyanate at 90°, giving the above carbamate. The compound crystallizes from ligroin and melts at 72°–73° to an oil. Nitrogen determination (Kjeldahl):

	Calculated for $C_{10}H_{11}O_2NCl_2$.	Found.
N	5.65	5.75

A mixture of this compound and β,β'-dichlorisopropyl phenylcarbamate (melting at 73°) melted at 58°–60°.

β,γ-Dibrompropyl Phenylcarbamate,

CH_2Br
|
$CHBr$.—β,γ-Dibrompropyl alcohol, which was pre-
|
$CH_2OCONHC_6H_5$

pared according to the directions of Michael,[1] reacted with

[1] THIS JOURNAL, **2**, 18.

phenyl isocyanate at 80°, giving a quantitative yield of the phenylcarbamate. It is very soluble in ether and insoluble in petroleum ether. When heated in a capillary tube it began to soften at 72° and melted to an oil at 77°–79°. A mixture of this compound and β,β'-dibromisopropyl phenylcarbamate melted at 55°–65°. Analysis:

	Calculated for $C_{10}H_{11}O_2NBr_2$.	Found.
N	4.15	4.00

NEW HAVEN, CONN.,
June, 1, 1910.

BENZOPHOSPHIDE.

BY P. N. EVANS AND JENNIE TILT.

A few phosphorus compounds, $RCOPH_2$, analogous to the acid amides, $RCONH_2$, have been prepared and studied. Those described in earlier publications include only the derivatives of monochloracetic acid,[1] dichloracetic acid,[2] and trichloracetic acid.[3]

In giving names to these compounds their analogy with acid amides has been properly emphasized by calling them acid phosphides, but it appears to the writers that this analogy is further best expressed by the names "monochloracetophosphide," etc., rather than "monochloracetyl phosphide," etc., as heretofore used; the name "benzophosphide," for instance, better expresses the idea that it is the acid phosphide of benzoic acid than "benzoyl phosphide," which might imply a phosphide (in the inorganic sense of a compound of phosphorus with another element or group) of the benzoyl radical. For this reason the name "benzophosphide" has been adopted.

To extend our knowledge of the acid phosphides to the aromatic compounds seemed desirable, and although its preparation has offered considerable difficulty on account of the extreme slowness of the reaction, benzophosphide, $C_6H_5COPH_2$, has been successfully made.

[1] A. Steiner: Ber. d. chem. Ges., **8**, 1178 (1875).
[2] P. N. Evans and C. H. Vanderkleed: THIS JOURNAL, **27**, 142 (1902).
[3] Cloëz: Ann. Chim. Phys., [3] **17**, 309 (1846).

Preparation of Benzophosphide.

Preliminary Experiments.—It is not necessary to give the details of the many attempts which proved either fruitless or at least very unsatisfactory; some brief notes will suffice.

Phosphine gas, PH_3, was prepared by heating together 50 grams of yellow phosphorus, 250 grams of potassium hydroxide, and 500 cc. of alcohol, and was stored in a gas holder. The gas, which consists of about equal quantities of phosphine and hydrogen and is not spontaneously inflammable, was passed into benzoyl chloride in test tubes or wash flasks, after being dried by passage through a long tube filled with lumps of dried potassium hydroxide. In some cases the gas was passed intermittently, for the sake of economy, in others the passage was continuous, and in some the apparatus was arranged to send the unabsorbed gas to a second gas holder, from which it could be passed again by merely reversing certain stopcocks.

In each experiment the liquid slowly became yellow, and then some deep yellow solid separated, probably solid hydrogen phosphide, and adhered to the glass. It was hoped and expected that the material treated with the gas would solidify as had been the case within a few hours in the preparation of dichloracetophosphide, but no such result was obtained during thirty days of contact with the gas.

The material was tested from time to time for evidences of the desired product, with positive results, as follows: The liquid was washed out with pure ether and allowed to evaporate in a desiccator containing both sulphuric acid and soda-lime, to absorb the ether and benzoyl chloride, respectively. A solid residue remained, partly insoluble in ether, the insoluble part giving qualitative tests for phosphorus with molybdate and with magnesia mixture after oxidation.

The amount of material obtained was not sufficient for satisfactory quantitative results; phosphorus estimations by the Carius method gave figures in approximate agreement with the calculated value, but also showed that an unusually long time and high temperature were necessary for complete oxidation to phosphoric acid; different analyses gave values

from 11.86 to 21.24 per cent. of phosphorus, the calculated value for the compound $C_6H_5COPH_2$ being 22.46 per cent.

Another method of preparation tried, but without any satisfactory results, was the bringing together of benzoyl chloride and phosphonium iodide at various temperatures.

The preparation was also attempted by treating the benzoyl chloride in a test tube with pure phosphine gas under pressure, liberating it in a side-neck test tube by letting water from a dropping funnel fall upon phosphonium iodide, removing moisture and hydriodic acid from the gas by contact with potassium hydroxide, and closing the circuit by connecting the exit tube of the test tube containing the chloride with the top of the dropping funnel, introducing a mercury seal about 50 cm. deep as a safety valve. The results of these experiments were similar to those already described, and did not seem to indicate any particular advantage in this method over the less laborious one of preparing the phosphine gas from phosphorus and alcoholic potash.

Final Preparation.—Six wash flasks containing in all 34 grams of benzoyl chloride were connected in series, and phosphine gas, made from phosphorus and alcoholic potash, passed slowly from a gas holder through a drying tube containing solid potassium hydroxide and then through the benzoyl chloride, for six weeks, about 30 liters of gas being used. The contents of all the flasks became somewhat yellow and then crystalline.

Fifty cc. of dry ether was added to the first flask, and then enough benzoyl chloride to dissolve all the crystalline material; the liquid was transferred to the second flask, more benzoyl chloride added as required, then transferred to the third flask, and so on.

The solution of the benzophosphide in ether and benzoyl chloride so obtained was filtered, and ether slowly added, with constant stirring, as long as any precipitation resulted. The faintly yellow crystalline precipitate was filtered off and washed with ether. On drying it formed a powder and weighed 10.5 grams.

The filtrate was allowed to evaporate to about half its orig-

inal volume in a desiccator containing both sulphuric acid and solid caustic potash; considerable solid separated, which after being filtered out and washed with ether resembled the original product except in being more nearly white, and weighed 5 grams, making a total yield of 15.5 grams.

Analysis of the Product.

Phosphorus.—Determinations by the Carius method showed that long heating was necessary. The following results were obtained:

I. 0.0733 gram substance, with 20 cc. of fuming nitric acid, heated 16 hours at 200°, gave 0.0582 gram $Mg_2P_2O_7$.

II. 0.0843 gram substance, with 20 cc. of fuming nitric acid, heated 24 hours at 200°, gave 0.0688 gram $Mg_2P_2O_7$.

	Calculated for $C_6H_5COPH_2$.	Found. I.	II.
P	22.46	22.10	22.72

Carbon and hydrogen were determined by combustion in a tube containing copper oxide and lead chromate. Great difficulty was experienced in effecting complete oxidation of the carbon. When heated in a porcelain boat, alone, complete burning of the charred material could not be effected in a current of oxygen. Mixed with copper oxide in the boat, and heated for 6, 10, 12, and 11 hours, respectively, in a current of oxygen, the results obtained were 53.70, 57.06, 55.64, and 59.17 per cent. of carbon, the calculated value being 60.87 per cent. In the last two cases, after heating for several hours in oxygen, the boat was withdrawn, and the contents ground with more copper oxide, the mixture replaced in the tube, and the heating in oxygen continued; in each case the potash bulbs gained in weight, but apparently the complete oxidation of the carbon had not been effected even under the extreme conditions described.

In five combustions of varying duration up to 12 hours in oxygen, the hydrogen results were as follows: 5.41, 6.05, 5.60, 6.04, and 4.59 per cent. The calculated value is 5.07 per cent.

Properties of Benzophosphide.

Prepared as described, it is a slightly yellowish powdery solid; in some experiments it was white. Under the microscope it appears as nearly spherical grains of fairly uniform size and strongly refractive.

On heating it shows no definite melting point, but gas bubbles begin to form and the mass to soften and contract at about 125°, continuing gradually up to 200°, and giving a rounded spongy mass. Heated in a current of dry nitrogen in a U-tube immersed in a bath, at 75° the issuing gas caused slight darkening of paper moistened with silver nitrate solution, indicating the evolution of phosphine gas, which was much more marked above 150°.

It is insoluble in water, and only slowly attacked thereby; exposed to moist air, phosphine is very slowly evolved, as indicated by the odor and the darkening action on silver nitrate paper.

It is easily soluble in absolute alcohol, but when reprecipitated by ether it is gummy and has apparently undergone some change.

It is insoluble in ether and in petroleum ether, but soluble in chloroform.

It is hoped to prepare other acid phosphides by similar reactions in this laboratory.

CHEMICAL LABORATORY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA,
June 4, 1910.

ON THE ACTION OF CHLORINE IN A SOLUTION OF CARBON TETRACHLORIDE AND OF CARBON TETRACHLORIDE ON METALLIC OXIDES.

BY ARTHUR MICHAEL AND ARTHUR MURPHY, JR.

Chlorine shows the property of uniting with many of the unsaturated nonmetallic oxides to form oxychlorides, and this has been found true also for several metallic oxides; for instance, molybdenum and tungsten dioxides. On the other

hand, Weber[1] states that stannous oxide glows when introduced into chlorine, forming, not an addition compound, but a mixture of stannic oxide and chloride. He also heated cobalt and nickel carbonates in chlorine and obtained the corresponding chlorides, but the conditions of the experiments render it impossible to decide whether the halogen acted on undecomposed carbonates or on the oxides formed previously by the action of heat. The primary object of this investigation was to ascertain the relation between the position of metals in the periodic system and the behavior of their unsaturated oxides towards chlorine. This was done for several of the metallic groups, but as these experiments were carried out about ten years ago and there is no prospect of completing the research, we thought it advisable to publish the results we obtained.

We have used in the following experiments a solution of dry chlorine in carbon tetrachloride.[2] If the tetrachloride is pure and dry, such a solution will keep indefinitely and its use has many advantages. The halogen is in a state of considerable concentration, and, as has been shown in organic reactions, is, generally speaking, more reactive than in a gaseous condition; the solution may be handled easily and the percentage, or concentration, of halogen may be determined without difficulty. In all of the following experiments we have used a sufficient amount of solution to furnish the halogen in considerable excess. With ferrous oxide the reaction goes with violence, even when the chlorine solution is cooled to —18°, ferric oxide and chloride being formed:

$$6FeO + 3Cl_2 = 2Fe_2O_3 + 2FeCl_3.$$

Manganous oxide also reacts energetically, but with less violence than ferrous oxide. Nickelous oxide reacts readily at room temperature, although to complete the reaction it is necessary to allow the mixture to stand some time. In order to complete the reaction with cobaltous oxide the mixture must be heated, in a sealed tube, to 100°. These three

[1] Jahres. d. Chem., **1861**, 147.
[2] Michael: J. prakt. Chem., N. F., **46**, 225.

reactions are perfectly analogous and may be represented as follows:

$$3MeO + \dot{Cl}_2 = Me_2O_3 + MeCl_2.$$

The relative facility with which these reactions proceed depends on the following relations: the affinity of the metal for chlorine, that of the monoxide for oxygen, and the energy required to separate the oxygen from the metal. On account of the greater affinity of iron than the other metals of this group for chlorine, of the easier reducibility of the monoxide of iron and its greater tendency to pass over into a more highly oxidized form than the other monoxides, it would have been safe to predict, once knowing that the reactions proceed in the above manner, that iron would show greater reactivity than manganese, cobalt and nickel monoxides. The data at hand do not permit, however, of drawing any safe conclusion in regard to the reactivity of the three last oxides among themselves, although there was a strong probability that manganese oxide would be the most reactive.

The behavior of stannous oxide is interesting. Liebig[1] prepared it by heating the oxalate to decomposition and obtained it as a brown substance. According to Vogel,[2] such a product may contain up to 4 per cent. of carbon dioxide and it is necessary to heat to redness in order to obtain a preparation completely free from dioxide. The stannous oxide thus prepared is grey. The brown stannous oxide, on addition to the chlorine solution, burns with small flashes, but the grey product reacts much more violently, the temperature rising considerably higher and the size of the flame being larger. This behavior seems anomalous, as one should expect the variety formed at the higher temperature, *i. e.*, the grey, to contain less energy and therefore to be less reactive, although it is possible that the presence of the small amount of carbon dioxide in the brown oxide may be connected, in some way difficult to understand, with the lesser reactivity. Stannic chloride is formed in each case and an insoluble, light brown oxide, which appears to be identical with the product pre-

[1] Ann. Chem. (Liebig). **95,** 116.
[2] Jahres. d. Chem., **1855,** 395.

pared by Schiff[1] by treating stannic acid with a solution of stannous chloride, and to which he assigned the formula $SnO,2oSnO_2$. In this case the reaction would be represented by the equation

$$41SnO + 4oCl_2 = 2oSnCl_4 + SnO,2oSnO_2.$$

Cuprous oxide is quite indifferent towards the chlorine solution, it being necessary to heat the mixture to 250° in order to effect a reaction. A dark brown, amorphous compound is formed, which has the composition Cu_2OCl_2. It appears, therefore, that we have here another instance of chlorine adding directly to a metallic suboxide to form an oxychloride. This cupric oxychloride, Cu_2OCl_2, has not been previously described, but a hydrated product has been obtained by the treatment of hydrated cupric chloride with calcium carbonate.[2]

Antimony trioxide reacts with the chlorine solution when heated to 100° in a sealed tube. The products of the reaction are soluble and consist of antimonic chloride and carbon oxychloride:

$$Sb_2O_3 + 3CCl_4 + 2Cl_2 = 2SbCl_5 + 3COCl_2.$$

The reaction, therefore, proceeds with the intervention of the solvent; indeed, antimonous chloride may be the primary product, since it is formed in the action of carbon tetrachloride on antimony trioxide at 100°. The action of chlorine and tetrachloride may be simultaneous, however, as we have found that the action of carbon tetrachloride on some metallic oxides is materially facilitated by the presence of chlorine. We also examined the behavior of some saturated metallic oxides towards the chlorine-carbon tetrachloride solution. The action of chlorine on such oxides was investigated by R. Weber[3] in the research already mentioned. His method was to pass the halogen over the oxide, which was heated to the temperature of the reaction. At a high temperature—red heat or above—Weber was able to convert all the metallic

[1] Ann. Chem. (Liebig), **120**, 52.
[2] Rousseau: Compt. rend., **110**, 1261.
[3] Jahres. d. Chem., **1861**, 148.

oxides he examined into the corresponding chlorides; even with substances so refractory towards chlorine as magnesium and aluminium oxides.

Silver oxide reacts with the chlorine-carbon tetrachloride solution at ordinary temperature, forming silver chloride and carbonyl chloride:

$$Ag_2O + Cl_2 + CCl_4 = 2AgCl + COCl_2 + Cl_2$$

This reaction is remarkable for several reasons. Carbon tetrachloride is an exceedingly stable substance towards double decomposition and no metallic oxide is able to replace two of its halogens under the conditions of the above experiment. With silver oxide we ascertained the temperature at which it yields phosgene gas with carbon tetrachloride alone and found it required heating to the neighborhood of 250° C. We are, indeed, accustomed to reactions in which the combined action of two chemical forces greatly facilitates a chemical change that proceeds with difficulty with one of them alone; for instance, the comparatively easy formation of silicon chloride from silica in the presence of carbon. This, however, is easily explained, since carbon shows a marked affinity for oxygen and we have, therefore, the two chemical forces, *i. e.*, the affinity of chlorine for silicon and of carbon for oxygen, assisting each other in overcoming the chemical hindrance to the reaction, which is the energy required to separate silicon from oxygen. In the reaction between silver oxide and chlorine-carbon tetrachloride, one of the reagents, carbon tetrachloride, contains in its own molecule the conditions for a double decomposition, since the carbon possesses an affinity for the oxygen and the halogen for the silver of the oxide. It is obvious, however, from the great difference between the reaction temperatures, that the presence of free chlorine materially assists the metathesis. An explanation of this appearance of chlorine as a catalyst may be found in assuming the formation of a "polymolecule"[1] consisting of oxide, tetrachloride and chlorine; in such a complex the com-

[1] Kekulé: Ann. Chem. (Liebig), **106**, 141. Michael: Ber. d. chem. Ges., **34**, 4028; **39**, 2140. This Journal, **39**, 3; **41**, 120.

bined *free chemical* energy[1] of the halogen atoms present would be far greater than that in the tetrachloride alone, and they should be able, therefore, to overcome the resistance involved in the separation of silver from oxygen at a lower temperature than the halogen in the tetrachloride by itself. In order to effect a reaction with lead oxide it is necessary to heat it with the chlorine solution to 100°. The tetrachloride does not enter into the reaction, which proceeds with the formation of lead peroxide and chloride:

$$2PbO + Cl_2 = PbO_2 + PbCl_2.$$

Mercuric oxide reacts readily with gaseous chlorine, even at 0°, forming chlorine monoxide and basic chloride. The ease with which this reaction proceeds depends, however, on the preparation of the oxide; the red oxide being comparatively inert, while with a precipitated, dry product the reaction is violent. We prepared mercuric oxide in the usual manner for making chlorine monoxide, that is, by precipitating mercuric chloride with caustic soda, carefully washing the precipitate and then heating to 300°. Although this preparation reacted readily at ordinary temperature with gaseous chlorine, and gave a good yield of chlorine monoxide, it showed itself indifferent to a 10 per cent. solution of chlorine in carbon tetrachloride. In fact, a reaction took place only when the mixture was heated to 100° in a sealed tube. The products formed under these conditions were of a variable nature; mercuric chloride and a mixture of basic chlorides, which we were unable to separate, were always present. There was no decomposition of the tetrachloride in the reaction.

Finally, we investigated the behavior of some of the oxides of the metals of the sixth group towards the chlorine-carbon tetrachloride solution, and also towards carbon tetrachloride alone, since it seemed of interest to ascertain whether chlorine exerts here a catalytic influence, as in other reactions. Watts and Bell[2] were the first to examine the behavior of carbon tetrachloride towards metallic oxides. They heated stannic oxide in

[1] See J. Am. Chem. Soc., **33**, 990.
[2] J. Chem. Soc., **33**, 442.

a tube to redness and passed over it the tetrachloride as vapor, obtaining stannic chloride in this way. A similar experiment with tungstic acid gave a mixture of tungsten dioxydichloride, WO_2Cl_2, and oxytetrachloride, $WOCl_4$, while titanic acid underwent no change. Later, Lothar Meyer,[1] apparently without knowledge of Watts and Bell's research, made analogous experiments, finding that the oxides of magnesium, aluminium and cerium are readily converted into chlorides, while those of boron, silicon, titanium and zirconium remain intact. Very recently, P. Camboulives[2] has published an exhaustive research on this subject, having examined the conduct of a large number of oxides towards the tetrachloride in a vapor condition, and determined the temperature at which the reaction proceeds. The oxides of most of the metals from the second to the eighth group, excluding those of the platinum family, which were not examined, were found to yield the corresponding chlorides.[3] Our experiments[4] with carbon tetrachloride differ from those mentioned above in that we heated the oxides with liquid tetrachloride in sealed tubes. Chromium trioxide reacts with the chlorine-tetrachloride solution at 150°, yielding chromyl chloride, CrO_2Cl_2, and carbonyl chloride, $COCl_2$; with the tetrachloride alone the same products are formed, but it is necessary to raise the temperature to 170°.

Molybdenum dioxide reacts with carbon tetrachloride at 250°, yielding the corresponding chloride ($MoCl_4$). Molybdenum trioxide reacts with the chlorine solution at 200° giving a yellowish green oxychloride, mixed with unchanged trioxide; at 225° mixtures of yellow and green compounds, which consisted probably of molybdenum dioxydichloride and oxytetrachloride, were formed. At 240° the replacement of oxygen is complete and the trioxide is converted into molybdenum pentachloride. In order to effect this reaction with tetrachloride free from chlorine it is necessary to heat the mixture

[1] Ber. d. chem. Ges., **30**, 682.

[2] Compt. rend., **150**, 175.

[3] Niobium pentoxide and thorium dioxide yield a mixture of oxychloride and chloride; tungstic oxide gave the oxychloride.

[4] They were made in the winter of 1899.

to about 280°. Liechti and Kempe[1] prepared molybdenum tetrachloride by heating the trichloride in carbon dioxide; the pentachloride by heating the metal in chlorine. While these preparations are apparently simple the chlorides are obtained pure with difficulty, and the method just described is probably the best way to make these compounds. Camboulives obtained the pentachloride by passing carbon tetrachloride vapor over heated molybdenum trioxide, but gives a very much higher temperature, *viz.*, 510°, as the reaction temperature. We found, too, that the oxide Mo_3O_8, with liquid tetrachloride, at 240° also gives the pentachloride. By heating tungsten trioxide with the chlorine solution either tungsten oxytetrachloride or tungsten hexachloride may be prepared according to the temperature. At 240° the oxychloride ($WOCl_4$) is formed; at 280° the reaction is complete and the hexachloride results. Without chlorine no action takes place at 240°, but at 280° the hexachloride is formed. These are probably the best methods to prepare the oxytetrachloride and hexachloride of tungsten. Camboulives, by his method, obtained only the oxychloride, and gives the high temperature of 560° as the temperature of reaction.

Finally, we made some experiments with the oxides of uranium. Uranium dioxide heated with carbon tetrachloride at 250°, for several hours, gives uranium tetrachloride. The oxides UO_3 or U_3O_8, at the same temperature, give the pentachloride. Roscoe[2] first prepared the pentachloride by heating any of the oxides of uranium with carbon in a current of chlorine, but the tetrachloride is formed at the same time, which makes it difficult to obtain a pure product in this way. Camboulives obtained a mixture of tetra- and pentachlorides from uranium trioxide and gives 360° as the reaction temperature. As the pentachloride loses chlorine easily, passing over into the tetrachloride, the pentachloride is probably the primary product of the reaction and suffers partially a decomposition into the tetrachloride at the high temperature of the experiment. The method here described is undoubtedly the best way for the preparation of these chlorides.

[1] Ann. Chem. (Liebig), **169**, 357.
[2] Ber. d. chem. Ges., **7**, 1132.

This method of preparing metallic chlorides by heating the oxides with liquid carbon tetrachloride may doubtlessly be extended and, in some cases, would probably be the best manner to prepare such substances; perhaps it could be used to prepare new chlorides. There is no doubt, also, that a more careful study of the conditions of temperature will make possible in many cases a gradual replacement of oxygen by chlorine, and thus furnish a good method of preparing oxychlorides.

EXPERIMENTAL PART.

Carbon tetrachloride absorbs, at 0°, about 25 per cent. of its own weight of chlorine, and at ordinary temperature about 10 per cent. Such solutions will keep indefinitely in properly closed vessels, providing the tetrachloride is pure and the reagents perfectly dry. The commercial tetrachloride may be easily purified for the above purpose by treating it in the sunlight with strong hydrochloric acid and powdered potassium chlorate, in a bottle with a loosely fitting glass stopper, adding more acid and chlorate as required and shaking the bottle occasionally. It is well to keep up this treatment for a number of days. The tetrachloride is then extracted with caustic soda, finally with water, and after careful drying with phosphorus pentachloride, distilled. It is also necessary to dry the chlorine finally by passing it through a tube containing the pentoxide. In the experiments where carbonyl chloride was formed, the tubes sometimes exploded and were always under considerable pressure. We found, however, that with the use of Jena combustion tubing an explosion rarely occurred. The tetrachloride solution used in the experiments described below contained from 8 to 10 per cent. of chlorine.

Ferrous Oxide.

Ferrous oxide was prepared by heating the oxalate in a combustion tube, finally to a dull red heat, and allowing the product to cool slowly in the gases of decomposition. There was some difficulty in transferring the oxide into a vessel containing the chlorine solution without oxidation. By pass-

ing a rapid stream of dry carbon dioxide, entirely free from air, through the combustion tube, and pouring the ferrous oxide into a flask containing the chlorine solution, which was cooled to —15°, and filled with carbon dioxide, it was possible to bring the two substances together without perceptible oxidation.

The reaction between ferrous oxide and chlorine is extremely violent; the oxide burns with a green flame, and considerable heat is evolved. The products of the reaction are ferric oxide and ferric chloride, both of which are insoluble in carbon tetrachloride. The tetrachloride was poured off and the products filtered and washed with dry carbon tetrachloride. The mixture was then dried in a vacuum to remove the tetrachloride and finally heated to constant weight at 100°. The ferric chloride was extracted with boiling water and titrated with 0.1 N silver nitrate for chlorine. The ferric oxide was weighed, dissolved in acid, reconverted into ferric oxide, and weighed again.

Weight of mixture, 1.2572 grams.

Weight of Fe_2O_3, 0.6260 gram; wt. of Fe_2O_3 (reconverted), 0.6258 gram.

Weight of $FeCl_3$, 0.6312 gram; weight of Cl, 0.4101 gram. Calculated, 0.4100 gram.

	Calculated.	Found.
Fe_2O_3	49.6	49.1
$FeCl_3$	50.4	50.1

Manganous Oxide.

The manganous oxide was prepared from the oxalate, like the ferrous compound, and in introducing it into the chlorine solution the same precautions are necessary. It reacts violently, burning with a bluish flame and with the evolution of considerable heat. The products of the reaction are manganic oxide and manganous chloride, both of which are insoluble in the tetrachloride. The precipitate was treated as described above in the case of ferrous oxide; the manganous chloride was separated from the oxide by boiling with water and

the "available" oxygen in the latter determined by the iodine method.

Weight of mixture, 1.1260 grams.

Weight of Mn_2O_3, 0.6308 gram. "Available" O: Found, 0.60 gram; calculated, 0.63 gram.

Weight of $MnCl_2$ (diff.), 0.4952 gram. Chlorine: found, 0.2855 gram; calculated, 0.2800 gram.

	Calculated.	Found.
Mn_2O_3	56.1	56.0
$MnCl_2$	43.9	43.7

Nickel Monoxide.

Nickelous oxide was prepared from dry carbonate by heating in a combustion tube until gas ceased to be given off, cooling to about 150°, and then passing over it a stream of dry hydrogen until the product was entirely cool. It reacted at ordinary temperatures with the chlorine solution, with a perceptible evolution of heat. The reaction is complete after standing for about an hour. The products, nickelous chloride and nickelic oxide, are insoluble in carbon tetrachloride, and were separated from the solution and prepared for analysis like the iron compounds.

Weight of mixture, 0.9632 gram.

Weight of Ni_2O_3, 0.5402 gram.

Weight of $NiCl_2$ (diff.), 0.4280 gram. Chlorine: found, 0.2301 gram; calculated, 0.2313 gram.

	Calculated.	Found.
Ni_2O_3	56.0	56.3
$NiCl_2$	43.9	43.8

Cobalt Monoxide.

Cobaltous oxide was prepared by heating the carbonate in a combustion tube. In order to effect a reaction with the chlorine solution it is necessary to heat in a sealed tube at 100°, and the action is complete only after several hours. The products of the reaction are cobaltic oxide and cobaltous

chloride, both insoluble in carbon tetrachloride. These were prepared for analysis as in the previous cases.

Weight of mixture, 0.7420 gram.

Weight of Co_2O_3, 0.4170 gram.

Weight of $CoCl_2$ (diff.), 0.3250 gram. Chlorine: found, 0.1752 gram; calulated, 0.1767 gram.

	Calculated.	Found.
Co_2O_3	56.2	57.0
$CoCl_2$	43.8	42.9

Stannous Oxide.

The two varieties of stannous oxide were prepared by heating the oxalate in a combustion tube and allowing the products to cool in the gases of decomposition. The brown product, formed at a temperature just sufficient to completely decompose the oxalate, is less reactive toward chlorine than the grey variety, which is formed at a heat approaching redness. Both modifications are stable in the air, but react with chlorine solution at room temperature, giving off heat and with a flame, the reaction with the grey oxide being the more violent.

The products of the reaction are stannic chloride and a higher oxide, which has probably the composition $SnO.2oSnO_2$. Stannic chloride is miscible with carbon tetrachloride, and cannot be completely separated from it by distillation. On fractionating, both products went over at temperatures from 76° to 114°, but at no time did either compound distil free from the other. The oxide $SnO.2oSnO_2$ is lighter in color than the oxide used in the reaction; that from brown stannous oxide being very light brown, and that from the grey oxide a light grey. When either variety was heated in the air, it added oxygen and formed stannic oxide. That the true formula of this compound is $SnO.2oSnO_2$, is by no means certain, but it certainly is an oxide containing a little less oxygen than the stannic oxide, although the difference is too slight to establish the constitution with absolute certainty.

The oxide was separated from carbon tetrachloride and stannic chloride by decantation, washing with carbon tetra-

chloride, removing traces of the latter by warming in a vacuum, and then drying at 100° to constant weight.

1.5825 grams $SnO.2oSnO_2$ gave 1.5990 gram SnO_2.

1.1260 grams $SnO.2oSnO_2$ gave 1.1329 grams SnO_2.

The amount of the product $SnO.2oSnO_2$ obtained from the amount of stannous oxide used was very close to the calculated amount:

2.5620 gram SnO gave 1.4350 grams $SnO.2oSnO_2$.

Calculated.	Found.
55.9	56.0

The formation of stannic chloride was shown by qualitative tests.

Cuprous Oxide.

Cuprous oxide, prepared by reducing a solution of copper sulphate with grape sugar, was dried in an air bath at 130° and then treated with the chlorine solution in a sealed tube. In order to obtain a reaction it is necessary to heat the tube to about 250°, when a dark brown amorphous compound is formed, which is the oxychloride, Cu_2OCl_2. This compound is insoluble in carbon tetrachloride and was separated and prepared for analysis as described above.

	Calculated.	Found.
Cu	59.4	58.4
Cl	33.1	33.8

Antimonous Oxide.

Antimonous oxide reacts with the chlorine solution to form carbonyl chloride and antimony pentachloride. The reaction does not take place at ordinary temperatures, but readily, and in a short time, in a sealed tube at 100°. The whole of the oxide was converted into the pentachloride, which is soluble in carbon tetrachloride, but is easily separated from it by fractionation.

With carbon tetrachloride alone, antimonous oxide reacts in a tube at 100° to form antimony trichloride and carbonyl chloride, but in order to complete the reaction it has to be

heated for 24 hours. Antimony trichloride is insoluble in carbon tetrachloride and was separated and prepared for analysis as described above.

0.4210 gram $SbCl_3$ gave 0.2629 gram AgCl.

	Calculated.	Found.
Cl	47.1	46.8

Camboulives,[1] by passing carbon tetrachloride vapor over the heated trioxide, also obtained the trichloride and gives 390° as the temperature of reaction.

Silver Monoxide.

Dry silver oxide was brought into the chlorine solution and the mixture allowed to stand for several hours, when the reaction was complete.

0.76 gram Ag_2O gave 1.084 grams AgCl, while the amount calculated is 1.086 grams.

With carbon tetrachloride alone the oxide has to be heated to about 250° in order to effect a reaction. The products are the same as in the presence of chlorine, *i. e.*, silver chloride and carbonyl chloride.

Lead Monoxide.

The reaction takes place at 100° in a sealed tube, and is complete after several hours' heating. Both the products formed, lead dioxide and lead chloride, are insoluble in tetrachloride.

1.7705 grams PbO gave 2.0517 grams of mixture; calculated, 2.0521 grams.

The chloride was separated by repeated extraction with hot water.

2.0577 grams substance gave 0.9525 gram PbO_2.

	Calculated.	Found.
PbO_2	46.3	46.4

Mercuric Oxide.

Mercuric oxide was prepared by precipitating the chloride with caustic potash, repeatedly extracting the precipitate

[1] *Loc. cit.*

with boiling water and drying at 250°. This product reacted with gaseous chlorine at room temperature and gave a good yield of chlorine monoxide. With the chlorine solution (9 per cent.) no action took place at ordinary temperature, and it was necessary to heat the mixture in a sealed tube at 100°. The tetrachloride is converted into phosgene gas, and the insoluble residue consists of a mixture of oxychlorides, varying in composition, as in different experiments they contained from 15 to 23 per cent. of chlorine ($HgCl_2$ = 26.1 per cent. Cl).

With tetrachloride alone the oxide reacts under the same conditions, forming carbonyl chloride and basic chlorides, containing, however, less chlorine (9 to 13 per cent.).

Chromium Trioxide.

Chromium trioxide reacts with the chlorine solution in a sealed tube at 150°, and forms the oxychloride, CrO_2Cl_2, and carbonyl chloride. Without chlorine, the tetrachloride is somewhat less reactive, a temperature of about 175° being required. The oxychloride is soluble in tetrachloride, but may be easily separated from it by fractionation.

Oxides of Molybdenum.

Finely powdered molybdenum dioxide, heated in a sealed tube for several hours to 250°, gave carbonyl chloride and a brown, microscopically crystalline powder. This substance was washed with tetrachloride and dried to constant weight in a vacuum. As shown by the following chlorine estimation, it consisted of molybdenum tetrachloride.

0.4253 gram substance gave 1.0251 grams AgCl.

	Calculated.	Found.
Cl	59.7	59.6

On heating molybdenum trioxide with the chlorine solution to 200° a reaction takes place, with the formation of phosgene gas and a yellowish substance, which, however, is usually mixed with some unchanged trioxide. On heating the mixture the yellowish substance sublimes, and, to judge from this and its other properties, it is the oxychloride MoO_2Cl_2. A number of tubes were heated at temperatures

between 200° and 225° for several hours, and gave mixtures of yellow and light green compounds containing chlorine, which probably consisted of the oxychlorides MoO_2Cl_2 and $MoOCl_4$.

By heating to 240° and maintaining this temperature for at least 3 hours, molybdenum trioxide is completely converted into pentachloride. This experiment was repeated a number of times, and we obtained each time a pure product, free from the oxychloride $MoOCl_4$, or any other chloride or oxychloride of molybdenum. The product melted at 194°–195°, and crystallizes from carbon tetrachloride, in which it is somewhat soluble, in fine, dark green, needlelike crystals, extremely hydroscopic, and rapidly changed by standing in air.

In order to remove the crystals from the tubes, these were opened and the crystals were washed several times with carbon tetrachloride in an atmosphere of dry carbon dioxide, drained off, and the last traces of the tetrachloride removed in a vacuum.

Molybdenum was determined in the following way: The pentachloride was dissolved in water and treated with hydrochloric acid and zinc. The compound is thus reduced to a salt of molybdenum sesquioxide, brown in color. Standard potassium permanganate was then added until the solution was colorless. Chlorine was determined by dissolving in water and precipitating with silver nitrate. The silver chloride was then filtered, dissolved in ammonia, and reprecipitated with nitric acid. The chlorine determinations are low, due perhaps to the treatment with ammonia and the subsequent precipitation. This is necessary, however, to remove any molybdenum trioxide or silver molybdate which may be formed.

1.2202 grams required 69.2 cc. $KMnO_4$.
0.2710 gram required 15.3 cc. $KMnO_4$.
0.4344 gram gave 1.1138 grams AgCl.
0.4971 gram gave 1.2861 grams AgCl.

	Calculated.	Found. I.	Found. II.
Mo	35.1	35.3	34.9
Cl	64.8	63.5	64.0

In order to effect a reaction between carbon tetrachloride, free from chlorine and molybdenum trioxide, it is necessary to heat somewhat higher (about 280°) and maintain this temperature for several hours. The products are the same as when chlorine is present, carbonyl chloride and molybdenum pentachloride, and the tetrachloride solution showed the presence of free chlorine.

At temperatures ranging from 200° to 250°, molybdenum trioxide and carbon tetrachloride behave in a peculiar manner. The trioxide, without changing its crystalline structure, turns blue, the intensity of the color varying with the temperature and the length of time it is maintained. This blue product is quite stable in the air, and is neither soluble in nor decomposed by water. On boiling with nitric acid it slowly dissolves, and in every case the solution showed the presence of chlorine, the amount varying as the intensity of the blue color. Thinking that this color was perhaps due to impurities in the carbon tetrachloride, we purified a fresh lot of this substance very carefully, but found the same results as before. It is possible that the blue color is due to carbon tetrachloride combining with molybdenum trioxide, and the presence of chlorine is due to the oxidation of the tetrachloride by nitric acid. Heated to 100°, the blue color gradually disappeared; heated to 200° it disappeared rapidly and molybdenum trioxide remained. The differences in weight of the product before and after heating were very slight and determinations of the halogen varied from a mere trace to over 3 per cent., but there was no indication of a constant percentage in any two of the products.

To obtain mixed haloids of molybdenum, we made some experiments using just enough carbon tetrachloride to remove oxygen from the trioxide and a large excess of bromine, but we invariably obtained molybdenum pentachloride.

Five-tenths gram molybdenum trioxide, 2.3 grams carbon tetrachloride, and 7–10 grams of bromine were heated in a sealed tube for several hours at 240°. Dark green, rectagonal crystals were formed, which showed the properties of molyb-

denum pentachloride. Qualitative tests showed no indication of bromine.

0.3194 gram substance gave 0.8365 gram AgCl.

	Calculated.	Found.
Cl	64.8	64.8

The oxide Mo_3O_8, prepared by reducing the trioxide in hydrogen, was heated in carbon tetrachloride, free from chlorine, for several hours at 240°. The product is molybdenum pentachloride.

Oxides of Tungsten.

Tungsten dioxide, heated for several hours in a sealed tube with carbon tetrachloride to 250°, is converted into tungsten tetrachloride. The substance agreed in its properties with the tetrachloride that Roscoe[1] obtained in the distillation of the pentachloride in carbon dioxide.

0.2018 gram substance gave 0.3501 gram AgCl.

	Calculated.	Found.
Cl	43.5	43.2

By heating tungsten trioxide in a solution of chlorine in carbon tetrachloride, either the tetraoxychloride and the hexachloride of tungsten may be obtained. Heated in a sealed tube to 190°–200° for three hours, a reaction took place, and the red, needlelike crystals of the oxychloride were formed. It melted at 208°.5–210° and was free from impurities. For analysis, the crystals were first washed with carbon tetrachloride and then, without removing them from the tube, heated to 160°. After some minutes, the tubes were removed from the bath and placed in a desiccator. The crystals were then dried to constant weight in a vacuum.

0.9280 gram substance gave 1.5640 grams AgCl.

	Calculated.	Found.
Cl	41.5	41.7

When tungsten trioxide is heated in the chlorine solution to 280°, and this temperature maintained for three to four

[1] Ann. Chem. (Liebig), **162**, 358.

hours, the replacement of oxygen by chlorine is complete and tungsten hexachloride results. It is possible to effect this reaction at a lower temperature, but the product is likely to contain some oxytetrachloride. In order to remove the crystals of hexachloride from the tube, and prevent decomposition, they were washed with carbon tetrachloride until free from phosgene, the tetrachloride drained off, and the tube placed in a bath and heated to 150°. The tube was then brought in a desiccator, filled with carbon dioxide, and the substance dried in a vacuum. According to Roscoe,[1] the hexachloride melts at 275°, but the presence of a trace of tungsten oxytetrachloride causes the melting point to be lowered to about 100°. The product we obtained melted at 275°, although it began to soften at 271°.

The analysis of the hexachloride was made by reducing the substance in hydrogen, passing the hydrochloric acid formed directly into silver nitrate solution, and weighing the silver chloride.

0.8455 gram gave 1.8230 gram AgCl.

	Calculated.	Found.
Cl	53.6	53.3

Tungsten trioxide reacts with carbon tetrachloride free from chlorine at 280°. Although a number of experiments were made at lower temperatures, we did not get the oxytetrachloride, but when the temperature was reached at which a reaction took place the hexachloride was formed at once.

The oxide W_3O_8, prepared by carefully reducing the trioxide in hydrogen, was heated with carbon tetrachloride, free from chlorine, for several hours at 240°. The tube opened under pressure with evolution of carbonyl chloride, and contained glittering black crystals. Under the microscope, two distinct varieties were noticeable; thin rectangular bundles of plates, and long, needlelike crystals, and in all probability a mixture of tungsten penta- and hexachlorides had been formed.

[1] Ann. Chem. (Liebig), **162**, 353.

Oxides of Uranium.

Uranium dioxide was heated in a sealed tube with carbon tetrachloride for several hours at 250°. The reaction results in the formation of the greenish brown tetrachloride and carbonyl chloride.

0.1500 gram gave 0.2260 gram AgCl.

	Calculated.	Found.
Cl	37.2	37.2

The oxides UO_3 or U_3O_8, heated in sealed tubes with the chlorine solution, or with carbon tetrachloride alone, gave in every case a mass of dark red crystals, consisting of uranium pentachloride. This compound is unstable; if heated it decomposes into the tetrachloride, the change being extremely rapid. In removing the pentachloride from the tubes, the crystals were washed with carbon tetrachloride until the washings were nearly colorless and free from carbonyl chloride, and the tube was then put in a desiccator filled with carbon dioxide and the carbon tetrachloride removed in a vacuum. When free from tetrachloride, the desiccator was again filled with carbon dioxide, and the crystals transferred from the tube to a porous plate. The compound was kept constantly in carbon dioxide.

0.4378 gram gave 0.7532 gram AgCl.

	Calculated.	Found.
Cl	42.6	42.5

OBITUARY.

STANISLAO CANNIZZARO.

With the death of Cannizzaro there has passed away the last of that group of men who made chemistry what it was during the middle of the last century.

Cannizzaro was born at Palermo, July 13, 1826, and died May 13, 1910. Therefore, during his long lifetime chemistry grew from comparative insignificance to its present development. During his early life Cannizzaro seems to have passed a more or less erratic existence. He matriculated at the

University of Palermo in 1841 as a student of medicine, being especially interested in physiology; meeting Piria, however, he soon turned from medicine to chemistry. His chemical studies were interrupted in 1848 by the Sicilian Revolution, in which he took part as an artillery officer and a member of the Sicilian Parliament.

When the revolution was suppressed Cannizzaro escaped to Marseilles and in 1849 to Paris. Here he met Cahours, who secured him a place in Chevreul's laboratory, where he began investigations with the assistant Cloez. While in Paris Cannizzaro attended the lectures of Regnault, who was at that time carrying out his investigations on the specific heats of the elements. The influence of Regnault on Cannizzaro was very great and lasted throughout his whole career.

In 1851 the first paper by Cloez and Cannizzaro on "The Action of Cyanogen Chloride on the Amides" was published, and in this same year Cannizzaro was called to a professorship of chemistry, physics and mechanics at Alexandria in Piedmont. He remained here until 1855, when he accepted a professorship in Genoa, where he remained until 1861, and where he wrote his famous "Sunto di un corso di filosofia chimica," which was published in 1858. In 1861 he went to Palermo, and in 1871 to Rome, where he remained until his death.

Let us now see what Cannizzaro did that placed his name among those of the foremost men of science of his day. Eighteen years before Cannizzaro was born Dalton had proposed the atomic theory and chemists began to determine the relative weights of atoms. A difficulty arose at once. The atoms of two substances often combine in more than one proportion, and there was no method then available for determining the *number of atoms of each* that had entered into combination.

A year after the publication of Dalton's "New System of Chemical Philosophy," Gay-Lussac announced his discovery of the simple volume relations in which gases combine, and in 1811 Avogadro proposed his well-known law. He distinguished between two kinds of minute particles—the *atom* and the *molecule*—the latter being usually made up of a group of the former. The atom was thus the ultimate unit, and the molecule was made up by a combination of these atoms. Avogadro announced that in equal volumes of all gases at the same temperature and pressure there are equal numbers of molecules. When we weigh equal volumes of different gases we are weighing equal numbers of molecules of these gases. Consequently,

the weights of equal volumes of gases give their relative molecular weights.

In all such cases we must, however, choose some unit, and Avogadro took as his unit of molecular weights the *molecule of hydrogen* and referred the molecular weights of all other gases to this.

The difficulty encountered by Dalton in determining the number of atoms of any given element that enter into combination was now frequently met with by working chemists in general and especially by Berzelius. Berzelius was engaged in the study of the composition of chemical compounds and in determining atomic weights. The only way in which he could see any escape from the difficulty first met by Dalton was to lay down certain empirical rules as to the number of atoms that enter into combination with one another, but this was, of course, of no permanent value and the whole atomic theory for a time fell into disrepute.

Chemists sought to escape from the difficulty by abandoning the conception of the atom altogether and using the term "combining weight," which meant the smallest weight of an element that combines with a unit weight of a given element. The result was that they soon had a number of "combining weights" for a given element and no means of determining which was the true value. The introduction of the word "equivalents" for combining weights met the same fate, as was bound to be the case, since they were simply words introduced where a clear idea was lacking.

Theoretical chemistry was thus beset by confusion, and the chemists of this period turned their attention rather to the discovery of fact than to generalization or the building up of a science of chemistry.

Faraday discovered benzene and found that it had the same percentage composition as acetylene, and Berzelius, in 1830, introduced the term "isomerism" and applied it to compounds having the same percentage composition, but different properties. Berzelius attempted to explain the "isomerism" of compounds and the "allotropy" of the elements as due to differences in arrangement of their minute particles or atoms.

Dumas, from a study of the replacement of hydrogen by chlorine, said that one "equivalent" of chlorine replaces one "equivalent" of hydrogen and laid stress upon the so-called "type theory." He, however, failed to distinguish between equivalent, atomic weight and molecular weight and thus added to the confusion.

Liebig and Wöhler published their work on the oil of bitter almonds and showed the importance and conduct of the group "benzoyl," thus accentuating the "radical" theory, which did not solve the problem in question.

Instead of aiding the upbuilding of a science of chemistry the work from 1830 to 1860 had apparently destroyed the generalizations of the earlier period. So apparently hopeless became the situation that chemists held a congress in Carlsruhe in 1860, with the object of trying to introduce, if possible, some order into theoretical chemistry, and it was here that Cannizzaro's great work was recognized. In 1858, as already stated, he had published his "Abstract of a Course of Chemical Philosophy," and copies were handed to members of the congress.

Cannizzaro here pointed out the correctness and importance of the generalization of his countryman Avogadro, but added, "Instead of taking for your unit the weight of an entire molecule of hydrogen, take rather the half of this weight, that is to say, the quantity of hydrogen contained in a molecule of hydrochloric acid."

Cannizzaro then showed how the molecular weights of compounds can be expressed in terms of half the molecular weight of hydrogen, and laid down the following generalization: "The different weights of one and the same element contained in the various molecules are always whole multiples of one quantity, which is justly called the atom, because it invariably enters the compounds without division." * * "In order to determine the atomic weight of any element, it is essential to know the molecular weights and the compositions of all or most of its compounds"—the molecular weights being, of course, determined by the use of Avogadro's law.

We can see what impression the "Abstract" made upon the congress by the following statement of Lothar Meyer: "Es fiel mir wie Schuppen von den Augen, die Zweifel schwanden, und das Gefühl ruhigster Sicherheit trat an ihre Stelle."

Cannizzaro thus recognized clearly, for the first time, the difference between molecule and atom. He showed that the apparent discrepancy between the results obtained by the law of Avogadro and that of Dulong and Petit was due to the fact that the former led to molecular weights and the latter to atomic weights, and that the two were in reality in perfect harmony with each other.

It would lead us far beyond the scope of this notice to attempt to point out even a few of the many consequences of Cannizzaro's work. He has been widely honored with mem-

bership in the various learned societies and academies of the world. He was made Senator in 1871. In 1872 he was chosen to deliver the Faraday lecture in London. He was elected an honorary member of the German Chemical Society in 1873, and in 1891 the Royal Society awarded him the Copley medal.

It was Cannizzaro who showed the chemical world the real significance of the generalization of Avogadro, and it is a noticeable coincidence that he should have been stricken down while honorary president of the Royal Academy of Sciences of Turin, which has undertaken to honor the memory of Avogadro by publishing a volume of his most important papers a century after the appearance of his epoch-making contribution to chemical science.[1]

Thus labored and passed away the man whom Ostwald characterizes in the lines: "In das Chaos der organischen Chemie seiner Zeit hat er begriffliche Ordnung gebracht."[2]

HARRY C. JONES.

REVIEWS.

INTRODUCTION TO PHYSICAL CHEMISTRY. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. New York: The Macmillan Co. 1910. pp. xv + 279. Price, $1.60.

This book is an abridged edition of the larger work of the same author, "The Elements of Physical Chemistry," which is so well and favorably known that this new text scarcely needs an introduction. The plan of presentation follows very closely that of the larger book, the matter merely being shortened by judicious omissions. The result fulfils the intention of the author of giving a text much more available for undergraduate instruction. It is nonmathematical in character, an unfortunate necessity in a book of this scope, and being written in the familiar original and live style of the author, it should prove one of the most successful of the elementary texts on the subject.

JOEL H. HILDEBRAND.

AN INTRODUCTION TO PHYSICAL SCIENCE. By FREDERICK H. GETMAN, PH.D., Associate in Chemistry, Bryn Mawr College. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. viii + 257.

The purpose of this book is unique. It is the author's belief that "the average student beginning the study of Chemis-

[1] For a fuller account of the work of Cannizzaro see the admirable article in "Science Progress," **5**, 147 by M. M. Pattison Muir, which was used in preparing this sketch.

[2] Z. physik. Chem., **71**, 384 (1910).

try has insufficient preparation in physical science. He can neither read his text-book intelligently nor attend a course of lectures on General Chemistry without having his attention diverted from the purely chemical side of the demonstrations by physical phenomena which he fails to understand. . . . . It is with the needs of this class of students in mind that the following pages have been written. . . . . The aim of the author has not been to compile a text-book of Physics but to bring together in logical order those physical principles which must be thoroughly understood by all who would become intelligent students of chemical science."

We are appreciating more and more, nowadays, the necessity of a thorough understanding of fundamental physical phenomena in order to gain an adequate insight into the more complex ones of chemistry. Many chemists of earlier training are lamenting a deficient knowledge of physics. By such this little book would be found instructive and entertaining reading. There is no doubt also that a review of it would be profitable for nearly every student of chemistry. In the college course, however, it is difficult to see just where it could be logically introduced. The student's course in physics should give him the training aimed at in this book. It will be interesting to hear of an instance where it has been worked into the course successfully. Whatever difficulties stand in its way for class-room work, it nevertheless deserves a hearty welcome from that large body of students who are forced to be more or less self-taught.

JOEL H. HILDEBRAND.

TECHNICAL CALCULATIONS FOR SUGAR WORKS. A Contribution to the Chemical Control of Sugar Manufacture. By OTTO MITTELSTAEDT, Technical Director of the Amstel-Suikeraffinaderij of Amsterdam. Translated from the third German edition by C. J. BOURBAKIS, Sugar Chemist. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1910. pp. xi + 117. Price, $1 50.

This little work, the original German third edition of which appeared some eight years ago, is a clear and remarkably compact explanation of a complete scheme of calculation for the chemical control of beet-sugar factories and refineries, the scheme being based on polarization, purity and ash data.

The translator has done his work well and produced a book which will prove a useful addition to the rapidly increasing library of books on sugar technology printed in this country.

The book is specially written for the guidance of the beet-sugar chemist. Much of the subject matter dealing with refining has to do with European methods and special products which are not used here. Of course the special factors of

beet practice are not applicable in cane-sugar control. The sole worth of the book to the practical man lies in the application of the formulae to his own work, but the data which suit only special European processes and conditions may mislead him. The book will prove useful and suggestive to cane-sugar chemists as well as those in the beet-sugar industry if read with due discrimination between principles and special applications. To such its value would have been enhanced, had the calculation data been expressed in the units of measure in use here.

One naturally looks for an index in a work so handy for quick reference. Perhaps the short text (117 pages) and well-arranged table of contents make an index unnecessary.

GEORGE W. ROLFE.

LABORATORY EXERCISES IN GENERAL CHEMISTRY. By WILLIAM MARTIN BLANCHARD, Professor of Chemistry, Depauw University. Easton, Pa: The Chemical Publishing Co.

This interleaved laboratory manual contains 66 well-chosen and well-described laboratory experiments. It contains no exercises on electrolysis or on dissociation, but is on the whole an excellent collection of laboratory experiments which could be used with any text-book. E. R.

E. MERCK'S ANNUAL REPORT OF RECENT ADVANCES IN PHARMACEUTICAL CHEMISTRY AND THERAPEUTICS. 1908. Vol. XXII. Darmstadt: E. Merck Chemical Works. 1909. pp. 394.

The Annual Reports of this firm are quite well known. They are simply a catalogue of medicinal substances and a brief statement of the published results of the past year collected from various sources. References to the literature are given. The whole collection is very useful for reference.

A. S. L.